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# **Computer model to generate predicted environmental concentrations (PECs) for antifouling products in the marine environment**

**2<sup>nd</sup> edition accompanying the release of Mam-Pec version 1.4**

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2<sup>nd</sup> Edition

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The development of the Mam-Pec model (version 1.2, released in 1999) was commissioned by the Antifouling Working Group of the European Paint Makers Association (CEPE) as subcontract within the project "Utilisation of more environmental friendly antifouling products", sponsored by the European Commission (DG XI; Contract # 96/559/3040/ DEB/E2). During 2001 and 2002 an update of the model (version 1.4) was prepared under contract to CEPE (2001-02-02).

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## Preface

The first proto-type version of the Mam-Pec model (version 1.2) was issued in 1999 as part of a study, commissioned by the European Paint Makers Association (CEPE) within the project "Utilisation of more environmental friendly antifouling products" of the Antifouling Working Group of the European Paint Makers Association (CEPE), sponsored by the European Commission (DG XI; Contract # 96/559/3040/ DEB/E2). Based on the experiences of users with the first version of the model, it was decided to upgrade the model to make it more flexible to regional country settings, to adapt some of the default exposure scenarios, to add an interactive module for concentrations in sediments, to revise and extend the help files, and to add a separate short manual. The Mam-Pec model has been or is considered to be used in admission procedures in different European countries. During 2001 and 2002 a second version of the model (version 1.4) was prepared under contract to CEPE (2001-02-02).

In close co-operation with members of the CEPE Antifouling Working Group revisions were implemented and beta test versions were evaluated. The authors greatly acknowledge the contributions of: J. Hunter (Akzo Nobel, International Coatings; chairman of the project review team), M. Perreira (Hempel), A. Jacobson and D. Baur (Rohm & Haas), B. Fenn and P. Turley (Arch Chemicals), C. Mackie (Compliance Services International), R. Wilmes and K. Schmidt (BASF),.

August 2002

## Preface to the 1<sup>st</sup> edition

The present study was commissioned by the European Paint Makers Association (CEPE) as one of the main components within the project "Utilisation of more environmental friendly antifouling products" of the Antifouling Working Group of the European Paint Makers Association (CEPE), sponsored by the European Commission (DG XI; Contract # 96/559/3040/ DEB/E2).

The work within the project was supervised on a regular basis by J. Hunter (Akzo Nobel, International Coatings), C. Nichols, D. Baur (Rohm & Haas), E. Kjaer, M. Perreira (Hempel), B. Koenig (Ciba), members of the Project Review Team of the Steering Group of the main project. Progress reports were presented at two Steering Group meetings, in which participated further M. Debois (EC DG-XI), W. Cortellini (EC DG-XI), M. Leonard-Williams (EC DG-VII), J. Cowley (EC DG-III), L. Perenius (EC DG-III), L. Sabatakakis (Ministry of Shipping, Greece), G. Wilson (UK-HSE), J. Chadwick (UK-HSE), C. Unger (KEMI, Sweden), P. Keymolen (CEPE), L. Tomasgaard (Nordox), S. Furtado (Sigma Coatings), S. Lintu (IMO secretariat), K. Rasmussen (EU-ECB), F. Runge (Norddeutsche Affinerie), and D. Arnold (Jotun-Henry Clark). Further contributions to the project were given by members of the CEPE Antifouling Working Group and others: A. Jacobson (Rohm & Haas), P. Turley (Arch Chemicals), C. Mackie (Cordah), J. Howcroft (HSE/WRC), P. Dollenmeier (Ciba), I. Kugler (Bayer), P. Lindgren (KEMI Sweden), C. Karman (TNO-MEP), Prof. J. Kemp (UK), and R. Pigot (Port of Rotterdam).

At Delft Hydraulics | WL the project was co-ordinated by A. Baart. B. van Hattum of IVM Vrije Universiteit was responsible for overall project management. Gratitude is expressed to the members of the Project Review Team, Steering Group, Antifouling Working Group, and all other persons involved at any stage of the project for their support and critical contributions to the project.

July 1999

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## Summary

Current risk-assessment models include only a limited number of emission, transport and chemical fate pathways required for a reliable assessment of the fate of antifouling products. This includes e.g. factors related to characteristics of the paint matrix (binding of biocide, leaching, erosion, life-time), shipping related factors (e.g. size, loading, speed, intensity, season in case of yachting marina), factors such as temperature, salinity or pH dependent characteristics and processes (biodegradation, speciation, sorption), and hydrological characteristics of typical marine environments. Only more sophisticated chemical equilibrium models are capable of a more comprehensive treatment of the subtle physico-chemical and biological processes and interactions. Especially for a sound comparison of different antifouling products it will be of importance that these processes and interaction-effects can be embedded in a risk-assessment model for antifouling products.

Commissioned by CEPE the Delft Hydraulics|WL (Delft, Netherlands) and the Institute of Environmental Studies/IVM (Amsterdam, Netherlands) have conducted a study in which a generic chemical fate model (MAM-PEC) for antifouling products was developed. This work was carried out as part of a larger project "Utilisation of more environmental friendly antifouling products" of the Antifouling Working Group of the European Paint Makers Association (CEPE), commissioned by the European Commission (DG XI; Contract # 96/559/3040/ DEB/E2).

Existing models were tested and their performance and shortcomings evaluated; this experience was then used to develop a new user-friendly computer model specifically for antifouling agents. The first proto-type version of the MAM-PEC model (version 1.2; 1999) provides a state-of-the-art prediction of environmental concentrations of antifouling products in five generalised 'typical' marine environments (open sea, shipping lane, estuary, commercial harbour, yachting marina). The user can specify different dimensions and area properties. Depending on these parameters different standard hydraulic scenarios can be generated. The model takes into account emission factors (e.g., leaching rates, shipping intensities, residence times, ship hull underwater surface areas), compound-related properties and processes (e.g.,  $K_d$ ,  $K_{ow}$ ,  $K_{oc}$ , volatilisation, speciation, hydrolysis, photolysis, bacterial degradation), and properties and processes related to the specific environment (e.g., currents, tides, salinity, DOC, suspended matter load).

Default QSAR approaches to estimate missing data are included. The accurate prediction of leaching behaviour and emission patterns constitutes a major source of uncertainties of the predictions. The model provides some default emission scenarios and the option to include more accurate scenarios based on shipping patterns, application data and leaching behaviour. For a selected number of compounds model-predictions for specific environments were compared with existing literature and monitoring data in order to evaluate the validity of the model. Based on the experiences of users with the first version of the model, it was decided to upgrade the model to make it more flexible to regional country settings, to adapt some of the default exposure scenarios, to add an interactive module for concentrations in sediments, to revise and extend the help files, and to add a separate



short manual. During 2001 a second version of the model (version 1.4) was prepared under contract to CEPE (2001-02-02). This second edition of the main report reflects the revisions made to the model and default scenarios and accompanies the release of MamPec version 1.4

## 1. Introduction

Fouling of the underwater area of ships with algae, other micro-organisms and small invertebrates has a serious impact on the operational costs of shipping, due to increased fuel consumption, and may lead to the introduction of non-endemic species in sensitive environments. Biocide-based antifouling paints are widely used to prevent fouling. Since the mid 1960s TBT has been applied in most antifouling paint systems. Due to serious effects observed in oyster cultures, coastal mollusc populations, and in some deep water snail species, many countries have banned the application of TBT-based paints on recreational boats and small vessels (< 25 m), or posed limits to acceptable leaching rates. Since that period various new products, usually based on copper in combination with an organic biocide, have been applied in the pleasure boating sector. Biocide-free coatings are being used on a limited scale or still in the testing phase. In some countries pilot experiments with small scale mechanical removal systems for small pleasure boats have been conducted.

During 1998 the Marine Environmental Protection Committee of the International Maritime Organization (IMO MEPC-42) adopted a resolution, aiming at further restrictions of TBT on large ships in 2003 (end of application) and 2008 (expected implementation of ban). It is expected that in the coming decade many new products will enter the market. In current admission and risk assessment procedures, antifouling agents are treated in a very generic way. Predicted environmental concentrations are derived with generic multimedia models, which do not account for the complex hydrodynamical processes in the marine environment. With the recently adopted Biocidal Products Directive by the European Commission and the expected IMO policies there is a need for the development of transparent and validated risk assessment strategies for these new products, acceptable for national authorities, industry, NGOs and other parties involved.

Against this background the Antifouling Working Group of the European Paint Makers Association (CEPE) has initiated a project "Utilisation of more environmental friendly antifouling products", commissioned by the European Commission (DG XI; Contract # 96/559/3040/ DEB/E2). Within that project an inventory was made of currently available antifouling products and their active ingredients. In addition, a computer model needed to be developed to estimate predicted environmental concentrations (PEC) for the active substances in various typical marine environments. Delft Hydraulics/WL and the Institute of Environmental Studies/IVM were subcontracted by CEPE to carry out the development of this computer model and its validation.

The project "Computer model to generate Predicted Environmental Concentrations (PECs) for antifouling products in the marine environment" was carried out according to project proposal P-97/42 and the contract of October 3, 1997 between CEPE and IVM.

The objectives of the study were:

- to provide a concise and critical review of relevant chemical fate models for contaminants currently used in marine risk assessment;
- to specify the requirements and specifications for a simple model for the prediction of antifouling products;

- to develop, refine and present a working 1D-computer model suitable for a set of pre-defined typical marine environments;
- to validate the model with existing monitoring data for a selected number of compounds.

In the next sections a brief survey is presented of relevant processes and factors determining chemical fate (Chapter 2) and emission characteristics (Chapter 3) of antifouling products. Existing models and their suitability is discussed in Chapter 4. In Chapter 5 a description is given of the main features of the model developed in this project and the argument behind choices and default values in the model. The manual to the MAM-PEC model is included in the helpfiles of the model, but will be included in the final version of this report in Chapter 6. A comparison of concentrations predicted by the model with values observed in monitoring programmes is presented in Chapter 7.

## 2. Environmental fate of antifouling products

Many complex and interacting processes that can be of a biological, chemical or physical nature determine the chemical fate of contaminants in the marine environment. Some of the major transport and transformation processes have been summarised in Table 2.1 and Figure 2.1. Especially in energy rich marine environments the hydrodynamic transport and mixing processes of water masses tend to have a major impact for most compounds. For compounds with a high affinity to particulate matter or sediment, sediment transport phenomena will be of dominant importance. Stable dissolved compounds are likely to be affected most by river discharges or tidal currents. In specific marine environments with low exchange rates or pseudo stagnant conditions the chemical and biological processes will become more important.

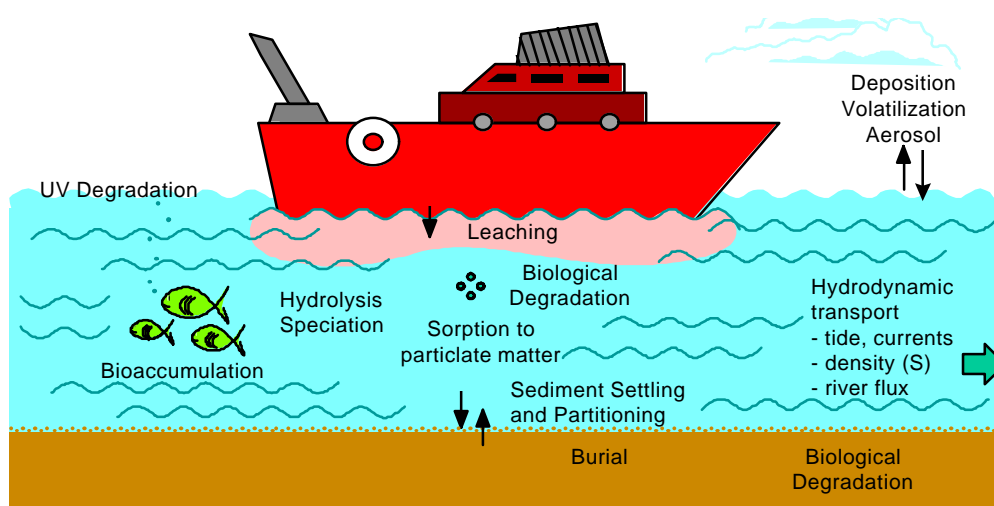


Figure 2.1 Chemical fate processes of antifouling products in the marine environment.

The relative importance of each of these processes is highly compound- and habitat specific and may vary between seasons. Biodegradation processes are highly temperature dependent and may be the dominant removal process in tropical water, while in temperate or polar zones this may be less. Photolysis may have a prominent role in the open sea even at greater depths in warm and transparent waters (Cooper *et al.*, 1987), while in turbid estuarine environment in temperate zones this only may be of importance in the upper water layers. Proper and realistic handling of photolysis in chemical fate models is complicated, as it varies with depth. This can only be done in adequate 3D models with proper relationships of effective rate constants with light penetration (transmittance or turbidity), temperature and binding to particulate matter and DOC.

There is a broad distinction between organic and inorganic compounds both in the mechanisms and relative importance of the processes. For instance for copper, processes such as sorption, speciation- and redox reactions have a prominent role in the fraction of

freely bioavailable and potentially toxic  $\text{Cu}^{2+}$  (Karman *et al.*, 1999). Among the trace elements mechanisms, partitioning and rate constants are highly element specific, and may depend strongly on the physico-chemical speciation. The speciation is highly dependent on environmental factors, such as salinity, pH, pE, particulate matter, presence and nature of ligand-substrates (Kramer, 1986). In contrast to the category of neutral hydrophobic compounds there are no simple and generic QSAR relationships with which speciation stability constants, partitioning and rate constants can be estimated. As copper is an ingredient in many antifouling products, a specific module covering the Cu speciation has been introduced in the MAM-PEC model.

Table. 2.1 *Transport and transformation processes determining the fate of chemical compounds in produced water. (Adapted from Miller, 1982, Mackay 1991).*

	Transport	Transformation
<b>Abiotic</b>	<i>Physical processes</i> Hydrodynamical transport Dispersion, diffusion Dissolution Emulsification Precipitation Sorption to particulate matter Sorption to dissolved org. matter Sedimentation Resuspension Burial Volatilisation Accumulation in microsurface layer Aerosol formation Atmospheric deposition (wet / dry)	<i>Chemical processes</i> Hydrolysis Photolysis Photo-oxidation Polymerization Complexation, speciation Dissociation Oxidation Reduction
<b>Biotic</b>	<i>Biological processes</i> Uptake, elimination Bioconcentration, bioaccumulation Excretion of biotransf. Products Food chain transfer Bioturbation	<i>Biochemical processes</i> Biodegradation in water (aerobic) Biodegradation in sediment (anaer.) Biochemical processes Biotransformation (Detoxification, hypertoxification)

### 3. Emission patterns of antifoulants

Emissions of antifouling products cannot easily be estimated. Usually the emissions are quantified as the product of a leaching rate ( $\mu\text{g}/\text{cm}^2/\text{day}$ ) and the total antifouled underwater area. The leaching rate depends on the type of compound, characteristics and age of paint matrix and velocity of the ship. The total antifouled underwater area depends on shipping intensities, dimensions of the various categories of ships, and many other factors such as cargo load and residence time of the various ships.

#### 3.1 Leaching rate

In a recent report of the CEPE Antifouling Working Group (CEPE AWG, 1998) a classification has been made of the various classes of biocidal antifouling coatings. The following types of coatings were identified: soluble matrix; insoluble matrix, TBT self-polishing copolymer and TBT free self polishing antifouling.

Both the soluble and insoluble matrix types contain copper oxide as the main biocide, with specific additional biocides (sometimes referred to as 'boosters') to prevent fouling from copper resistant fouling species. With typical in-service periods of 12-18 months, the biocide-release rate decreases exponentially during the lifetime of the coating. After the in-service period the release rate drops below the critical level needed to prevent fouling.

Both the TBT self polishing copolymers and TBT free self polishing paints, which both may contain copper, have a different biocide release pattern. The biocide release rate show a rapid decrease in the first months to year, followed by constant release rate during the remaining in-service period of up to 5 years. The velocity of the ship has a strong impact on the leaching rate.

Experimental determinations of leaching rates usually are conducted by manufacturers during the development and testing phases of new products, usually according to ASTM protocols. The results from these experimental studies cannot be translated to real-life leaching rates from ships to which the product is applied. Available protocols have been criticised by various authors (Berg, 1995). For many of the new products established and certified analytical methods are hardly available (Thomas, 1998). To date, no field studies with painted ships have been published in the open literature.

Leaching rate estimates used in a brief selection of recent experimental or risk-assessment studies have been summarised in Table 3.1. For each compound a broad range of leaching rate estimates is observed. Copper leaching rates usually are higher than for other compounds. Leaching rates reported for TBT usually are below regulatory implied values of  $4 \mu\text{g}/\text{cm}^2/\text{day}$  in some countries (USA, Sweden). A comprehensive review leaching rates was beyond the scope of this study.

Table 2-1: Summary of leaching rate estimates reported from various studies

Compound	Leaching rate $\mu\text{g}/\text{cm}^2/\text{day}$	Type of study	Author
TBT	4	North Sea	Stronkhorst <i>et al.</i> (1996)
	2.5	Marina	Johnson and Luttik (1996)
	0.1 – 5	Harbour	Willingham and Jacobson (1996)
	1.3 – 3.0	Ships > 25m	Lindgren <i>et al.</i> (1998)
Cu	6.2	Marina	Matthiesen and Reed (1997)
	1-20	Not specified	Hare (1993)
	8 – 25	Ships >12m	Lindgren <i>et al.</i> (1998)
	37 – 101	Ships > 25m	Lindgren <i>et al.</i> (1998)
	4 – 6 *	Exp. Studies	Berg (1995)
Irgarol	2 – 16	Marina	Ciba (1995)
	5	Marina	Scarlett <i>et al.</i> (1997)
	2.5 – 5	Exp. Studies	Thomas <i>et al.</i> (1999)
Sea-Nine 211	1 (0.1 – 5)	Harbour	Willingham and Jacobson (1996)
Zinc Omadine	3.3	Exp. Studies	Thomas <i>et al.</i> (1999)
Diuron	0.8 – 3.3	Exp. Studies	Thomas <i>et al.</i> (1999)
Dichlofluanid	0.6 – 1.7	Exp. Studies	Thomas <i>et al.</i> (1999)

\* after 21 days. During the first 21 days leaching rates ranged between 7 – 61  $\mu\text{g}/\text{cm}^2/\text{day}$ .

Based on expertise available within the CEPE Antifouling Working Group, it was decided that the following values would be used as default leaching rates in the MAM-PEC model:

Copper	50 $\mu\text{g}/\text{cm}^2/\text{day}$
TBT	4 $\mu\text{g}/\text{cm}^2/\text{day}$
Other biocides	2.5 $\mu\text{g}/\text{cm}^2/\text{day}$

In the default scenarios the leaching rate for moving ships and ships at berth were taken similar because of the large uncertainties in the presently available data. Similarly, an option to mimic the expected decrease patterns in leaching rate during the in-service time of the coating, was not included in the MAM-PEC model.

### 3.2 Emissions from commercial ships in harbours

The total emissions from yachts and commercial vessels depend on the specific local shipping patterns, such as number of ships, port arrivals, time in port, and type and dimensions of ships. The total wetted hull surface of a ship further depends on the cargo load and weather or sailing conditions.

General shipping statistics can be obtained from various sources (ISL, 1997) or commercial services from Lloyds Register Ltd and other companies (e.g. MaritimeData Ltd). National authorities or local port authorities have yearly publications of port-arrivals for various categories of ships. Although traffic intensities and port arrivals are monitored on a large scale in European waters, there is no structured and aggregated reporting system covering all European waters, similar as in the Cost 301 study (Cutland *et al.*, 1987). In Table 3.2 port arrivals in the Rotterdam harbour area are listed, obtained from the on-

line Harbour Information System (<http://www.port.rotterdam.nl/>) and annual reports (Port of Rotterdam, 1998). Related data for other European ports can be obtained via the International Association of Port and Harbours (IAPH) or the European Sea Ports Organisation (ESPO) or from internet sites of local ports ( links via the IAPH website <http://www.iaph.or.jp>).

Table 3.1 Port-arrivals in some major European harbours<sup>1</sup>

Port-arrivals 1996	Europe	Arrival or Total <sup>2</sup>	average size in DWT	max depth
Helsinki	4413	T*0.5	7144	11
Le Havre	6890	A	21735	29
Hamburg	11679	A	5021	
Piraeus	26330	A	2351	
Genoa	7479	A	14074	
Barcelona	7200	A	12642	16
Rotterdam	25078	A	14797	
Amsterdam	8756	A	6900	
London	14177	A		
Felixstowe	7157	A	15057	13.5
Average	11916		11080	

<sup>1</sup> Source: ISL (1997). <sup>2</sup> Statistics for total (T, sum of arrival and departure) were converted to arrivals ( $0.5 * T$ )

One of the problems encountered during the study was that port statistics are not kept on a standardised basis. Shipping dimensions may be based on length, depth, dead-weight tonnage (DWT), gross tonnage (GRT/GT), net tonnage (NRT/NT), and compensated gross tonnage (CGT). Some ports only provide statistics on cargo landed in, cargo tonnage (weight or capacity), no. of containers, revenue tons (in US), freight tons, or e.g. harbour tons. Large variations exist also in the ship categories mentioned in the different reporting systems. The generally accepted Lloyds classification is presented in Appendix I.



*Table 3.2 Ship arrivals of sea-going vessels at the port of Rotterdam by length class, 1996 - 1997.*

Class of length	1997		1996	
	Number	GRT/GT*	Number	GRT/GT
11 - 100	13,930	27,050	14,305	27,426
101 - 150	6,220	47,652	6,179	47,114
151 - 200	5,932	119,092	5,593	114,239
201 - 250	1,394	52,406	1,378	53,171
251 - 300	1,782	106,468	1,666	98,525
301 - 380	349	45,481	295	40,187
Total	29,607	398,149	29,416	380,662
Ship movements of sea-going vessels	82,912		82,313	

\* Unit: GRT/GT x 1000 tons; source: Port of Rotterdam (1998).

Other classification and aggregation systems can be found in e.g. ISL (1997) and Times (1989). The large differences in dimensions and proportions of current commercial ships, make that tonnage dimensions cannot easily be translated to length, wide, depth and surface area related dimensions. For some individual categories of ships (such translation formulas have been described in e.g. ISL (1997). Based on the database from the Port of Rotterdam, a plot was made of length categories (10 m class width) against DWT (Figure 3.1). The regression power-function has a high explained variance (over 90%), but as can be seen from the error bars, using this type of formulas for conversions may introduce significant variation, ranging to well over 100%. A similar plot for length against depth over all shipping categories has similar broad confidence intervals.

During the project specialists from International Paint surveyed available data on surface area antifouled for 19 (Lloyds) vessel types from a large database (Dataplan). DWT data were retrieved versus underwater hull area. The antifouled surfaces were split into three sections: flat (bottom), underwater sides, and the boottop area (area antifouled but not permanently immersed - the waterline area). In Appendix II an example is given for the category of reefers (specialised dry cargo vessels). For approximately 300 ships in the database figures for the underwater sides and the flats were available. For only 160 ships additional data were available for the boottop area. The figures clearly demonstrate that even with a specific category a large variation in surface area is present and that the regression statistics show a low explained variance (with  $R^2$  ranging from 1 to 15%).

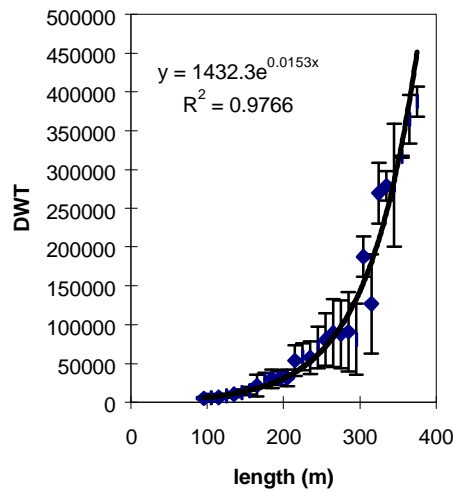


Figure 3.1 DWT (mean +/- stand. dev.) for different length categories of ships arrived in 1997 in the Port of Rotterdam ( $n = 29,600$ ).

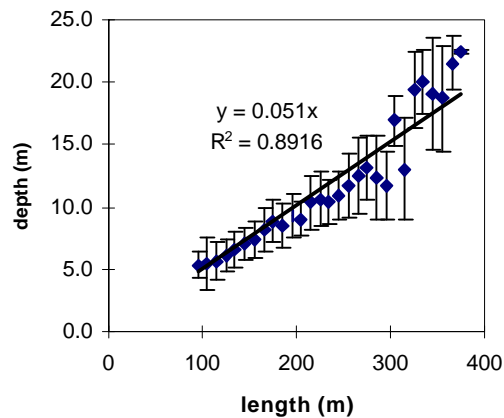


Figure 3.2 Depth (mean +/- stand. dev.) for different length categories of ships arrived in 1997 in the Port of Rotterdam ( $n = 29,600$ ).

The estimation from DWT-based regression relationships may easily lead to deviations of up to 300% from actual measured values.

As both underlying port statistics were hardly available and as the estimation based on a statistical survey of antifouled surface areas would not result in improved uncertainty intervals, it was decided that the wetted hull surface would be estimated with a simple approximate geometrical model. Similar approaches have been applied in related studies.

In an emission inventory study on TBT in Dutch waters by TNO (Willemssen and Ferrari, 1992) an average antifouled area of 4000 - 5000 m<sup>2</sup> for all size classes was used. In the US modelling study predicting Sea-Nine concentrations with the EXAMS model for Sea-Nine (Willingham and Jacobson, 1996) the estimation of the wetted hull surface for ships in the New York Harbor was based on average dimensions of nine ship types (219 m length and 33 m width). The average width of US ships in New York Harbor is 14.1%. Based on a simple geometrical model the average wetted hull area was taken to be equal to:

$$\text{Surface area submersed (m}^2\text{)} = \text{length (m)} * \text{breadth (m)} * 1.3. \quad [3.1]$$

In a preliminary stage of the project the ship outer surface was approximated as a simple box. Assuming that on average 50% of the box is underwater, than the surface area anti-fouled can be calculated from the length (L), width (W) and depth (D) as:

$$\text{Surface area submersed (m}^2\text{)} = L * (W + D) + (W * D) \quad [3.2]$$

As a first approximation the width and depth of the ships were taken as 15% and 5% of the length respectively, roughly matching with the dimensions of sluices and port facilities in Dutch harbours. The depth estimate is in close agreement with the dimensions of ships arriving in Rotterdam Harbour in 1997, as indicated in Figure 3.2. The average submersed and antifouled surface areas for the different length classes were calculated with equations 3.1 and 3.2 and are indicated in Table 3.3. Both methods yielded reasonably matching surface area estimates. For reasons of comparability the calculation proposed by Willingham and Jacobson (1996) was adopted for the MAM-PEC model.

*Table 3.3. Estimated dimensions and surface area submersed calculated with two simple geometrical models.\**

Class of length M	nr of ships in 1997	Average Length M	Width (15%) m	Depth (5%) m	Estimated area antifouled m <sup>2</sup> Eqn. [3.2]	Estimated area antifouled m <sup>2</sup> Eqn. [3.1]
11 - 100	13,930	45	6.75	2.25	420	397
101 - 150	6,220	125	18.75	6.25	3242	3061
151 - 200	5,932	175	26.25	8.75	6355	5999
201 - 250	1,394	225	33.75	11.25	10505	9917
251 - 300	1,782	275	41.25	13.75	15692	14814
301 - 380	349	340	51	17	23987	22645

- Calculated with Eqn. [3.1](based on New York Harbor ship dimensions) and Eqn. [3.2] (box-model based on Dutch port dimensions).

As it clear that the surface estimation has a large uncertainty, it is recommended that in further studies a more refined approach (based on statistical surveys as indicated in Appendix II) is followed. Combined with detailed port or shipping statistics (specified according to the Lloyds categories indicated in Appendix I) this should provide a basis for a more reliable estimation of the submersed surface area.

The time spent by ships in harbour and the time spent manoeuvring in ports further determine the total emissions. This may vary by category and type of ship and be variable.

Based on data provided by the Rotterdam port authorities an average residence time of 3 days was used in the MAM-PEC model and time spent manoeuvring at arrival and departure was taken as 3 hours. In the Exams study reported by (Willingham and Jacobson, 1996) a residence time of 2 days was used for the New York Harbor.

Another factor introducing large uncertainties in the emission estimation is the market share of the specific product studied, determining the fraction of ships to which the product is actually applied. In a review by Anderson (1993) a world wide distribution (Japan excluded) of 69 % TBT-based self-polishing paints, 16 % TBT free self-polishing paints and 15 other products is mentioned for 1993. For alternative products, market shares are usually not communicated for commercial reasons. When currently proposed IMO protocols will become adopted, the use of TBT is expected to be diminished or banned during the first decade of the 21<sup>st</sup> century. The market share of other biocide-based antifouling paints or biocide-free systems will become more important. With currently existing differences in admission policies and regulation between countries, this may even vary on a local scale. Especially for the categories of smaller ships (In many countries TBT is not allowed on ships <25 m) a reliable estimation of the usage patterns of alternative products, and prediction of expected environmental concentrations is extremely difficult. In the MAM-PEC model this is circumvented by the introduction of an application factor (% of ships to which the product is applied) for each length category.

### 3.3 Emissions from yachts in marinas

For the estimation of emissions from yachts specific models have been proposed by Johnson & Luttik (1994) and Baur & Jacobson (1996). In marinas for pleasure crafts the density of ships present is highly season-dependent. In both cited studies, the estimation starts with the yearly averaged number of yachts present in the harbour, and the average painted area per ship. Based on an assumed fraction of boats on which the specific product is applied (i.e. market penetration of the specific product; default set at 100 %) the total area antifouled with the product is calculated. In combination with the leaching rate of the specific product the total emission of the product in the harbour is calculated. Typical starting values from the studies Johnson and Luttik (1994), based on middle sized Dutch marinas, and Baur and Jacobson (1997), based on French Mediterranean marinas, are indicated below in Table 3.4. As the average yacht length in Dutch marinas is not representative for other countries, it was decided to take the Golfe Juan Marina as model for the prototype marina in the MAM-PEC model.

Table 3.4 Typical settings for emission estimation in pleasure boat marina.

Input Parameter	Unit	Marina-1 Dutch Marina	Marina-2 Golfe Juan	Marina-3 Antibes
Emission estimation				
- nr of berths		250	841	1230
- ships at berth (35%) <sup>1</sup>	#	89	299	437
- ships moving	#	0	0	0
- antifouled area per ship <sup>2</sup>	M <sup>2</sup> / ship	5	22.5	25.5
- application factor <sup>3</sup>	%	100 %	20 %	20 %
- leaching rate <sup>4</sup>	µg/cm <sup>2</sup> /day	2.5	2.5	2.5

<sup>1</sup> This is derived in the models of Johnson and Luttk (1994) and Bauer and Jacobson (1997) from the year-averaged fraction of boat slips used (100 % in summer, 25 % in winter; overall 50%) and the average fraction of yachts present in the harbour (71%), i.e. not sailing or dry docked.

<sup>2</sup> Values taken from Bauer and Jacobson (1997) set as 50 % of boat deck area.

<sup>3</sup> In model of Bauer and Jacobson (1997) default value for application set at 20%

<sup>4</sup> Default value as in Johnson and Luttk (1994) and Bauer and Jacobson (1997)

Based on practical experience the following formulas have been recommended in commercial brochures by some paint suppliers for yachts (Akzo Nobel / International Paint / Sikkens) for the estimation of the underwater surface of pleasure crafts:

motor-launch	low draught	$A = LWL * (W+D)$
sailing-yacht	intermediate draught	$A = 0.75 * LWL * (W+D)$
sailing yacht	deep keel	$A = 0.5 * LWL * (W+D)$

A= undewater area; LWL= length at water line; W= width; D= depth

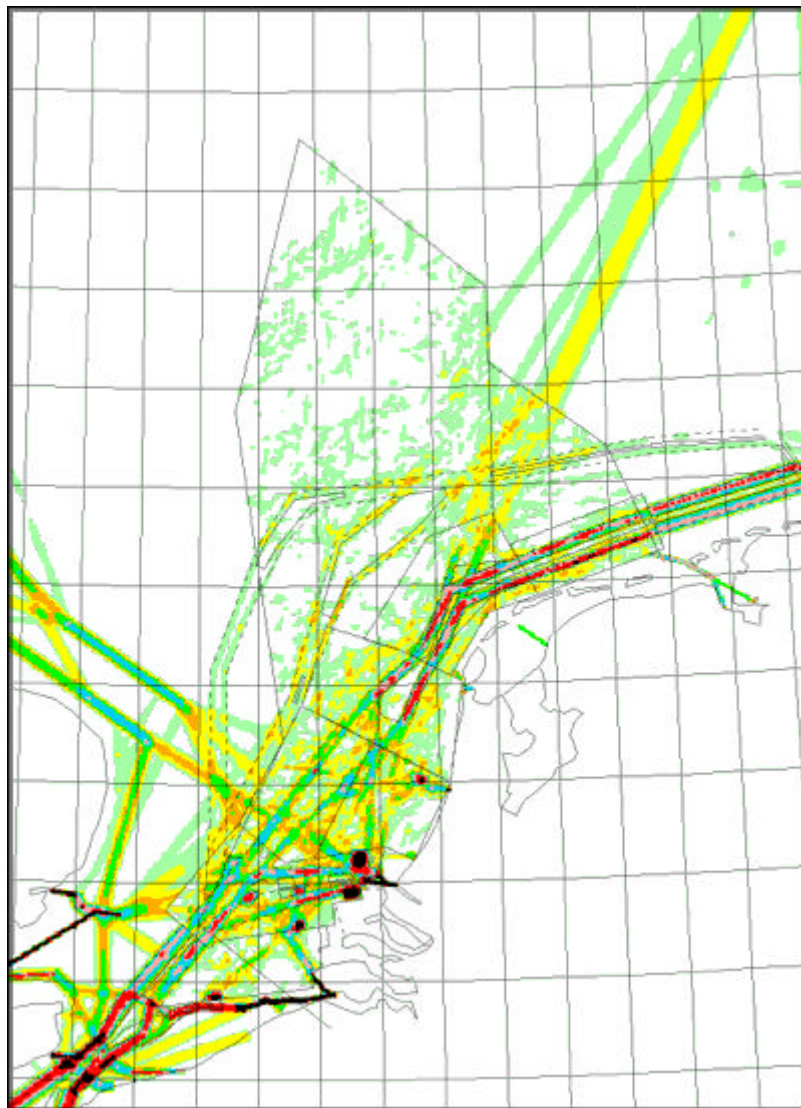
### 3.4 Emissions from ships at open sea and shipping lanes.

Shipping patterns on the open sea are monitored by national authorities. Much of this surveillance is executed in the framework of marine safety. An overview of organisations involved is available in IMO (1998). Similar as to port statistics hardly any aggregated studies have been published, which could be used as a starting point for the present modelling study. The data presented in Times (1989) were too general to be of use, but provide information on shipping intensities in other parts of the world.

In a recent Dutch policy document (Min VW – DGG, 1996) an analysis was made of shipping patterns on the Dutch section of the North Sea. This area has one of the highest shipping densities of the world (260,000 ship passages per year), with ships passing through the Brittish Channel with destination to Belgian, Dutch, German and Scandinavian ports. The main traffic is bound to obligatory shipping lanes (IMO, 1996). At any time of the day an average number of 390 ships is present in the area. In Figure 3.3 the density distribution in the area (in nr of ships per 1000 km<sup>2</sup>) during 1995 is presented with densities ranging from 1-3 ships in the Northern area up to 27-45 ships in the main shipping lanes and the Straight of Dover, and to over 45 ships in the vicinity of large harbours (Antwerpen, Thames Estuary and Port of Rotterdam). The figure was derived from the material presented at the internetsite site of DGG:

[www.minvenw.nl/dgsm/dichttrg.htm](http://www.minvenw.nl/dgsm/dichttrg.htm). In Table 3.5 the different categories of vessels are indicated.

Similar information for other European waters could not be retrieved within the scope of the present study. As detailed statistics were available for the Dutch section of the North Sea, and as additionally the hydrology of the area is well known, it was decided to use this area as proto-type environment for the present study. A section of the German Bight of (100 x 10 km with an average depth of 20 m), along the Northern Dutch Coast was taken as a first model for the shipping lane. The length class distribution and average wetted hull surface areas per ship category according to Table 3.3 used, as such information was not available for the area.



*Figure 3.3 Density plot of ships (average number of ships per 1000 km<sup>2</sup> present at any time of the day) crossing the Dutch Continental Shelf area in 1995. Densities in shades of gray ranging from 1-3 ships in the Northern area up to 27-45 ships in the main shipping lanes in the Southern Bight and the Strait of Dover, and to over 45 ships in the vicinity of large harbours (Antwerp, Thames Estuary and Port of Rotterdam). Fishery ships, dredging vessels and other non port-bound ships are not included. Original density plots in colour can be consulted on-line at <http://www.minvenw.nl/dgsm/dichtrg.htm>. Source: Min VW – DGG (1996).*

*Table 3.5 Distribution of shipping traffic on the Dutch section of the North Sea (1995). Indicated are average number of ships present at any time in the total area (41,785 km<sup>2</sup>).*

Category	Average number of ships				%
	South sector	Deep Water route	North sector	Total	
General cargo	97.2	8.6	15.2	120.9	31.3 %
Tanker	28.9	2.7	5.2	36.8	9.5 %
Bulk cargo	15.2	2.2	1.7	19.1	4.9 %
Container	8.6	0.6	1.0	10.2	2.6 %
Passenger ferries	2.6	0.2	0.5	3.3	0.9 %
Fisheries	85.4	19.6	42.7	147.6	38.2 %
Recreational	8.8	0.4	0.7	9.8	2.5 %
Others	29.6	2.9	6.3	38.8	10.0 %
Total	276.3	37.1	73.2	386.6	100 %

Source: Min VW-DGG (1996).





## 4. Suitability of existing environmental models

During the last decade a large number of chemical fate models has been developed and reported in the literature, ranging from simple, generic steady-state models, used for screening studies (Cowan *et al.*, 1995) to highly complex dynamic chemical fate and hydrodynamical models, to be used for more realistic simulation trials (Mackay *et al.*, 1991; Trapp and Matthies, 1997; WL, 1996). Existing chemical-fate models may be classified according to:

- type of chemical (neutral, polar, super lipophilic);
- number and nature of compartments to be included (one-compartment versus multi-media models);
- type of partitioning, transport and transformation processes to be included (Level 1-III);
- ability to allow for physico-chemical speciation of compounds;
- ability to allow for covariation of parameters with environmental conditions (e.g. pH, temperature or salinity dependent rate- or partitioning constants);
- generic models versus region or compound-specific models;
- spatial resolution (1,2 and 3-D models);
- temporal resolution (steady state versus dynamic models);
- ability to link with hydrodynamical or biological productivity models.

The following preliminary selection was made of available models in the period before the development of the first version of the Mam-pec model (1997-1999), and that were considered for its potential applicability to PEC calculations of antifouling compounds in the marine environment:

- ECOS 2.1.4, Plymouth Marine Laboratories (UK; Harris *et al.*, 1993); Test version of ECOS 3 available in 1<sup>st</sup> half of 1998.
- Exposure Analysis Modeling System-EXAMS II, version 2.96 (US-EPA, Burns, 2000; Willingham and Jacobson, 1996).
- Fugacity based EQC-Model, Level I, II and III (Equilibrium Criterion Model) of the Environmental Modelling Centre, Trent University (Canada) (Mackay, 1991; Mackay *et al.*, 1996).
- QWASI, fugacity-based model (Ling *et al.*, 1993).
- TOXFATE 3.6, National Water Research Institute, Canada Centre for Inland Waters (Halfon and Allan, 1995).
- EUSES 1.00, JRC, Environment Institute - European Chemicals Bureau (ECB, 1997).
- Danish Chemical Fate Model, fugacity-based level III (Severinsen *et al.*, 1996).
- Antifouling Box Models: Johnson-Luttik model (Johnson and Luttik, 1994), Baur-Jacobson model (Bauer and Jacobson, 1997).
- DELWAQ 1994, multi dimensional chemical fate / water quality model (Delft Hydraulics, 1994; WL, 1996).
- CHARON, model for water chemistry and speciation (De Rooij, 1991).
- CHARM, hazard assessment and risk management model (TNO, Karman *et al.*, 1996).

Table 4.1 Models evaluated for suitability to predict environmental concentrations of antifoulants.

Programme	Authors, Institute, Corp.	Available	Operational
ECOS 2.1.4	Plymouth Marine Laboratories (UK)	+	+
EXAMS II - 2.96	US-EPA, CEAM, Athens GA (USA)	+	-
DELWAQ/CHARON	WL   Delft (Netherlands)	+	+
EQC	EMC, Trent Univ. (Canada)	+	+
Luttik-Johnson	RIVM (Netherlands)	+	+
Jacobson-Bauer	Rohm & Haas (US, France)	+	+
TOXFATE 3.6	CCIW-NWRC (Canada)	-	-
Dan.Chem.Fate Model	IESE, NERI (Denmark)	-	-
EUSES 1.00	ECB (Italy)	+	+
QWASI	Univ. of Toronto (Canada)	-	-
CHARM	TNO (Netherlands)	-	+

The models to be evaluated should meet most of the criteria mentioned below and should be able to accommodate the main features of the emission patterns and environmental processes that are deemed important for antifouling agents. The realistic incorporation of the different types of antifouling systems (Flemming *et al.*, 1996; Peterson, 1992), the shipping characteristics (intensity, tonnage, age), and the relative usage of the specific products will be important factors. Advantages and disadvantages of these models and possibilities for adaptation were assessed, based on the following main criteria:

- ability to simulate the 5 standard environments, with simple hydrodynamic characterisation of these environments;
- allow for variation of typical emission patterns of antifouling products (different paint systems, leaching characteristics, shipping characteristics);
- inclusion of main processes and compartments determining chemical fate;
- compatibility with data from existing scientific and legislative databases of compound properties (because of this preference is given to concentration-based models above fugacity-models);
- conformity to accepted EU, OECD protocols for risk assessment of chemicals;
- standardised input (default values, administration of parameter values);
- user-friendly; model to be used without assistance of highly trained personnel.

Review of these existing models (Table 4. 2) revealed that most, if not all, were deficient in their treatment of parameters specific to marine antifouling paints, e.g. leaching rate of biocides, shipping related factors (e.g. type, size, loading, speed, intensity, season in case of yachting marina), temperature, salinity, pH dependent characteristics and processes (biodegradation, speciation, sorption), and hydrodynamic characteristics of typical marine environments.

Current generic risk-assessment models usually include only a limited number of emission, transport and chemical fate pathways required for a reliable assessment of the fate of antifouling products. Only the more sophisticated chemical equilibrium models, with both steady state or dynamic calculation options (EXAMS, ECOS, DELWAQ, QWASI, TOXFATE) are capable of a more comprehensive treatment of the subtle physico-chemical and biological processes and interactions. For an environmental risk assess-

ment it is important that these processes and interaction-effects can be embedded in the model.

*Table 4.2 Suitability of available models before the development of the first version of the Mam-pec model (1997-1999).*

	C/f	Nr. of Media	Hydro Dynamics	Emiss. from ships	Skills required	Effect of S,T,pH	Generic	Dimensions	Steady state / Dynamic
EUSES	c	4	-	-	low	-	g	1D	s
EQC-based models	f	> 4	-	-	low	-	g	1D	s
QWASI	f	> 4	+	(+)	high	(+)	l	2D	s/d
TOXFATE	f	> 4	+	(+)	high	(+)	l	2D	s/d
Johnson and Luttik '94	c	3	-	(+)	low	-	g	1D	s
Baur and Jacobson '96	c	3	-	+	low	-	g	1D	s
EXAMS	c	> 4	+	+	high	(+)	g	3D	s/d
ECOS	c	> 4	+	+	high	+	g	3D	s/d
CHARM	c	3	(+)	-	low	-	g	1D	s
DELWAQ	c	>3	+	+	high	+	g	3D	s/d

Explanation: C/f: concentration or fugacity based model; Nr. of Media: number of abiotic main and subcompartments included (watercolumn, sediment, air, soil, particulate matter); Hydrodynamics: ability to cope with more complex marine hydrodynamic features; Emiss. from Ships: ability to allow for typical emission patterns. Generic: generic model (g) or location specific (l). - : missing; + : option is available; (+): option is partly available.

Only a few of the generic models generic can easily provide a spatial resolution (2D or 3D) of the final results (EXAMS, ECOS, DELWAQ) which is of importance for estuarine environments with strong gradients.

From the generic 2D models, both ECOS and DELWAQ can easily be adapted to complex estuarine hydraulic processes. For the EXAMS models this can only be achieved after linking with tailor-made and location specific calculation modules. The DELWAQ model has previously been linked to hydraulic models for the North Sea (Waterloopkundig Laboratorium, 1995; Baart and Boon, 1998). It can easily be linked with general water chemistry and biology models (CHARON) or dedicated estuarine sediment transport models, such as SILTHAR (Delft Hydraulics, 1995), which have been used successfully for several large international harbours (Port of Rotterdam, Hong Kong).

The evaluation prior to the development of Mam-pec version 1.2 confirmed the initial assumptions at the start of the project, that none of the currently available generic models could be used directly for a realistic treatment of the chemical fate processes of antifouling compounds, and that a new modelling instrument needed to be developed.

In a simultaneous study, commissioned by the Health and Safety Executive in UK a special model was developed for British estuaries, the REMA model (HSE, 1999) in the period 1996-1999. It is based on the QWASI model and contains 3 sections of an estuary with three adjacent marinas. Hydrodynamic exchange rates between marinas and estuarine sections need to be entered manually. The model does not allow an estimation of the hydrodynamic exchange processes. The treatment of the chemical fate processes is in many respects similar to the first version of the Mam-Pec model. Several default estuaries are included in the model. The model has been validated successfully for these estuaries. The treatment of emissions is not flexible, fixed surface areas are included in the model for pleasure crafts and medium sized ships. The REMA model is limited to typical estuaries in the UK and cannot easily be adapted to other exposure scenarios as proposed by the CEPE Antifouling Working Group.



## 5. Background to the MAM-PEC Model

### 5.1 Requirements of the model

The primary aim of the generic model is a state-of-the-art prediction of environmental concentrations of antifouling products for a wide range of marine environments.

The specifications for the model, as suggested by the CEPE antifouling working group, state that the model should derive environmental concentrations of antifouling products in a number of generalised ‘typical’ environments. The model must also be able to account for differences in temperature, salinity, pH, hydrodynamics, and chemical and physical processes.

During Phase-I of the project the required specifications were evaluated with the project review team and discussed with the Steering Group. Based on this consultation the main features of the required specifications the model could be summarised as:

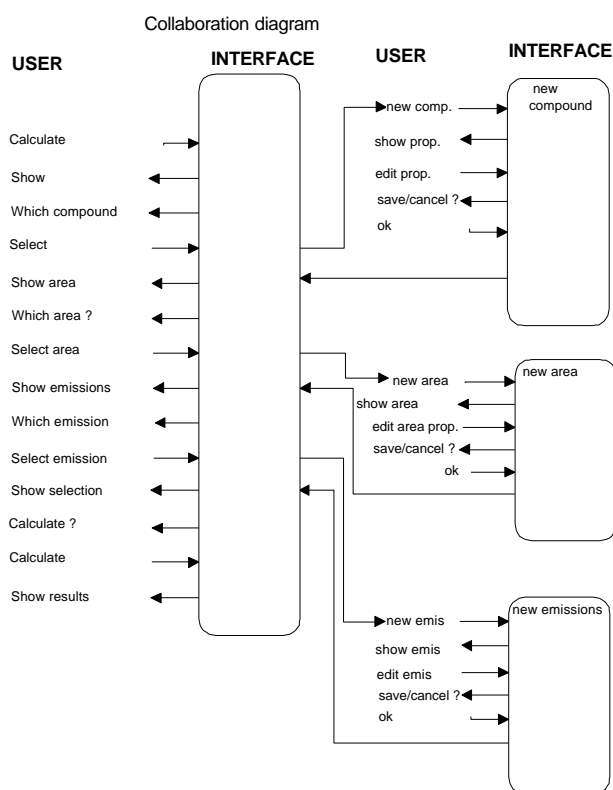
- inclusion of 5 prototype environments, adaptable to local conditions, with relevant hydrodynamics and gradients;
- capability to handle typical antifoulant emission patterns (shipping patterns, leaching behaviour, application scenarios);
- relevant chemical fate processes should be included standardisation, acceptability;
- ability to handle different classes of compounds and variation in properties (metals, neutral or polar organic substances);
- compliance with risk-assessment approaches within EU, OECD, IMO;
- suitable for end-users with moderate skills, robustness of modelling software;
- model to be suitable for common desktop/laptop PCs under Win95;
- working with model via a graphical User Interface (Windows ‘look and feel’), for workflow management, database access, presentation and handling of results;
- two dimensional hydraulic and environmental modelling framework behind UI: DELWAQ-2D, SILTHAR, optional for links to CHARON.

### 5.2 General structure and user interface

The basic structure of the MAM-PEC model is indicated in Figure 5.1. A central User Interface (UI written in Windows Visual Basic 4.0) guides the user via different list boxes, menus and screens, and helps to provide the required input settings for 1) (prototype) environments; 2) compound properties, and 3) emission scenarios. User supplied information is stored in Access type databases (MS Access 7.0), which are shielded from the user. Interaction with the databases is through the User Interface. From the UI various modules are called upon for the calculations of water quality and hydraulic exchange and transport processes (DELWAQ and SILTHAR programmed in Fortran). The calculations are executed on a user-defined grid basis. The User-Interfaces main screen allows the user to compose the input for MAM-PEC and to run its computational part, or view, print or file results from previous runs.

Each combination of environment, compound and emission scenario is assigned automatically a unique identifying label, in order to keep track of the different runs of the

model. Basic sets of (read-only) default settings for the prototype environments and default emission scenarios are provided for reasons of standardisation and can be used for comparisons between different compounds.



*Fig. 5.1 Basic structure of the user interface of the MAM-PEC model. Collaboration diagram demonstrating the basic interactions between the user and the user interface.*

### 5.3 Prototype environments

In the initial stage of the project a choice was made between a generic model for a few standard environments (with flexibility for adaptation to mimic local conditions) or a region-specific model (based on e.g. existing models for North Sea, Baltic, Mediterranean). Some pros and cons of the two options are indicated below.

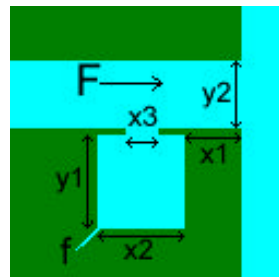


*Advantages/disadvantages of generic vs. region-specific models.*

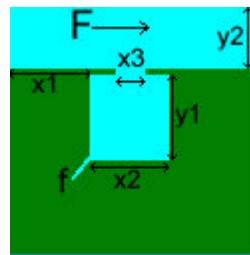
Criterion	(1) generic	(2) region-specific
adaptation to other regions	relatively easy	only with large effort
Standardisation	relatively easy	complex
skills required of user	moderate	high
expected acceptance by users (e.g. EU,IMO, CEPE members)	+	-
realism of prediction	order of magnitude estimate	more accurate prediction, but only for the given region

Given the uncertainties in the emission estimations (Chapter 2) the limited realism of generic models was not considered as problematic.

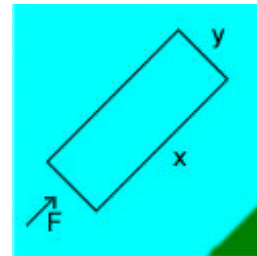
The following generic prototype environments were built into the model: commercial harbour, estuary with small harbour, marina, open sea and shipping lane. Examples of the prototypes are given in Figure 5.2.

**Examples of prototype environments**

**Commercial harbour**  
**Estuarine harbour**



**Marina**



**Shipping lane**  
**Open sea**

*Figure 5.2 Examples of the prototype environments included in the MAM-PEC Model. Symbols are explained in Table 5.1.*

The commercial harbour is situated along a large estuarine river at a distance of 2 km from the mouth of the river. The estuarine harbour is similar and differs in dimensions and the size of the harbour. The marina is an enclosed area situated directly at the coast. An additional poorly flushed marina was added as a default scenario to mimic conditions with low tidal exchange (e.g. Baltic, Mediterranean). Both marina, commercial and estuarine harbour may have additional flushing from a small river or urban drainage system discharging at the rear end of the harbour (indicated with f Figure 5.2).

Table 5.1 *Prototype environments. Default settings for input parameters for harbour layout dimensions, hydrology and water quality.*

Parameter	Symbol	Unit	Commercial Harbour	Estuarine Harbour	Marina*	Open Sea Shipping Lane
<b>Water quality</b>						
Silt concentration	$C_{pm}$	mg/L	35	35	35	5
Temperature	T	°C	15	15	20	15
Salinity	S	‰	30	34	34	34
Part. Matt. Org-C	POC	mg/L	1	1	1	0.3
Dissolved Organic Carbon	DOC	mg/L	2	2	2	0.2
PH	pH	-	7.5	7.5	8	8
Background concentration	C	mg/L	0	0	0	0
<b>Sediment</b>						
Nett sedimentation velocity	$v_s$	m/day	1	1	0.5 (1)	0.2
Sediment density	$\rho$	kg/m <sup>3</sup>	1000	1000	1000	1000
Thickness mixed layer	$\delta$	m	0.2	0.2	0.1	0.1
Fraction organic carbon	foc	-	0.03	0.03	0.03	0.01
<b>Hydrology</b>						
Tidal period		hour	12.41	12.41	12.41	12.41
Tidal height		m	1.5	1.5	1 (0)	0
Tidal current	F	m/s			1 (0.2)	1
River flow velocity	$F_{riv}$	m/s	1.5	1		
River width	$y_2$	m	500	500		
Width coastal area	$y_2$	m			400	
Depth of river		m	20	15		
Density difference		kg/m <sup>3</sup>	0.8	0.4	0.1	
Flush in harbour	f	m/s	0	0	0	
Density difference of flush		kg/m <sup>3</sup>	0	0	0	
<b>Harbour lay-out</b>						
Distance from mouth	x1	m	2000	1000		
Length	x2	m	10000	5000	400	
Width	y1	m	2000	1000	400	
Depth of harbour		m	20	15	3.5	
Harbour entrance width	x3	m	5000	2500	100 (50)	
Harbour entrance depth		m	20	15	3.5	
Height dam harbour entr.		m	0	0	0	
Width dam harbour entr.		m	0	0	0	
Exchange rate (% per tide)		%	65	80	4.3 (1.8)	
<b>Area open sea</b>						
Length	X	m				20000
Width	Y	m				10000
Depth		m				20

\* Between brackets: default marina - poorly flushed

The shipping Lane and Open Sea scenarios were derived from conditions in the Dutch Continental Sector of the North Sea.

The hydrology in the harbours is determined by river flushing, tidal action and/or density differences between the water masses. The dimensions of potentially present submersed dams or locks at the harbour mouth (e.g. in areas with large tidal differences) can be specified. The relative dimensions of the hydrological characteristics and harbour layout and dimensions (input variables are indicated in Table 5.1) strongly affect the overall exchange volumes. Estuaries may have complicated stratified hydrodynamics, a fresh or brackish top layer moving out to the sea and a salt water wedge moving upstream. The stratification strongly affects the trapping of suspended matter into the sediment and the related cycling of pollutants between river and sea. The model SILTHAR, which was specially developed by Delft Hydraulics to simulate sediment dynamics and water exchange processes in estuarine harbours (WL, 1995), was applied to provide a realistic calculation of water exchange volumes and transport of particulate matter. In Appendix III an overview is given of how the exchange processes estimated with SILTHAR have been implemented in the MAM-PEC model. The hydrology of the open sea and shipping lane environments is dominated by residual currents.

Based on the dimensions chosen for the environments the DELWAQ module in MAM-PEC creates a grid. For the harbours this is a 10 x 10 grid. For the river and coastal sections the number of grid cells depends on the dimensions defined in the input screen. The size of the grid cells is derived from the dimensions of the harbour. The MAM-PEC model further defines a flow field, based on the dimensions provided by the user. This flow field determines the exchanges between the different grid cells.

For each of the cells in the grid separate hydrological and chemical-fate calculations are being executed. The net overall exchange of the harbour/marina area is calculated based on the settings provided and represented in the environment screen as  $\text{m}^3/\text{tide}$  and % exchange per tidal cycle.

The user has the option to overrule the calculated water exchange rates, as this parameter may have been determined in specific local studies.

The prototype environments exhibit marked differences in water quality parameters. Coastal and estuarine environments have much higher concentrations of suspended matters, DOC and nutrients compared to the open sea, and usually have strong gradients in salinity. The salinity gradients have a marked effect on density-driven exchange processes in estuaries, mobilisation of suspended matter-bound contaminants and speciation of trace elements. In the model the salinity gradient is constructed with a parameter describing the density difference between river water and seawater. An overview of input variables and default settings for water quality and sediment parameters of the prototype environments is listed in Table 5.1.

The five default environments cannot be changed or edited by the user. The user has the option define new environments to adapt to specific situations. Each environment is

given a new name and the settings are stored in the environment tables of central database. Via pop-up menus existing environments can be selected and if necessary edited.

## 5.4 Compound properties and chemical fate calculations

In the second input panel the compound properties are being entered. Compound settings are being stored in the compound table of the central database. The basic set of properties that need to be provided is indicated below. For ease of input, several options have been included to convert dimensions to the actual dimensions used by the model. For the degradation processes the user may provide either  $DT_{50}$  based values (half-life in days) or rate constant bases values ( $\text{day}^{-1}$ ), which are actually used in the model.

The input parameters for the chemical processes modelled in the MAM-PEC model are similar as in the well known EUSES (1996). The user is recommended to make use of validated and properly evaluated sets of physico-chemical data, available for many existing compounds in general databases such as EINECS, AQUIRE, DOSE, AQUAPOL, publications such as Mackay *et al.* (1997), Howard and Meylan (1997), or specific databases such as the CLogP Starlist for  $K_{ow}$ . Criteria for the evaluation of the quality of such data have been documented extensively in most of the above cited publications and the Technical Guidance Documents (TGD, 1996) supporting the EC risk assessment directive (93/67/EEC) and regulation (EC 1488/94) of new and existing chemicals. As evaluated data usually are available for the products to be modelled with MAM-PEC from prior notification or admission procedures, no options are provided in MAM-PEC to assist in the quality assurance of the input data.

*Substance specific parameters required by the model are:*

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- molecular mass ( $M_w$ , g/mol)
- aqueous solubility ( $S_w$ ) at 20 °C ( $\text{g/m}^3$ )

for organic compounds :

- vapour pressure ( $P_v$ ) at 20 °C (Pa)
- partition coefficients:  $K_{oc}$ , BCF, and/or  $K_{ow}$  for organic micro pollutants
- Henry's constant (H) at 20 °C ( $\text{Pa.m}^3/\text{mol}$ )
- (bio) degradation rate constants at 20 °C specified as:
  - watercolumn photolysis ( $\text{day}^{-1}$ )
  - watercolumn abiotic (hydrolysis) ( $\text{day}^{-1}$ )
  - watercolumn biodegradation ( $\text{day}^{-1}$ )
  - sediment abiotic degradation ( $\text{day}^{-1}$ )
  - sediment biodegradation ( $\text{day}^{-1}$ )

for heavy metals :

- partition coefficient  $K_d$  ( $\text{L.kg}^{-1}$ )

for estimation of missing values partition coefficients (organic compounds):

- melting temperature ( $T_m$  in °C)
  - Proton dissociation constant (pKa);
- 

Leaching rates are not only compound specific, but further depend on characteristics of the paint matrix, velocity of the ship and other factors. Leaching rate data are therefore being entered in the model via the emission input-panel.

When only very limited physico-chemical data are available (e.g.  $T_m$ ,  $S_w$ ,  $M_w$ ,  $P_v$ ,  $pK_a$ ), a few optional calculation and QSAR modules are available for calculation of  $K_{ow}$ ,  $H$  and  $K_{oc}$  of . It should be noted that these options only provide a very rough order of magnitude. For instance for the estimation of  $K_{ow}$ , much more sophisticated QSAR based systems are available such as CLogP and similar systems. Recently available software from US-EPA, such as the EPIWIN suite (Meylan and Howard, 1999), combines database functions and property-estimation software. Reviews of available and accepted chemical property estimation techniques have been described in e.g. Nendza and Hermens (1996), Lyman *et al.* (1990), TGD (1996), Howard and Meylan (1997), and Boethling and Mackay (2000). Whenever available, the user should make use of reviewed and certified data, according to the recommendations in TGD (1996). The following calculation modules have been implemented, and can be called upon via the compound input screen:

#### **Approximation of octanol-water partition coefficient $K_{ow}$**

(Isnard and Lambert, 1989; Lyman *et al.*, 1990)

$$\text{For } T_m < 25 \text{ }^\circ\text{C: } \log K_{ow} = 4.62 - 0.72 \log(1000 S_w)$$

$$\text{For } T_m > 25 \text{ }^\circ\text{C: } \log K_{ow} = 4.81 - 0.77 [\log(1000 S_w) + T_m - 25]$$

#### **Calculation of Henry's Law constant $H$**

$$H = M_w \cdot P_v / S_w$$

#### **Estimation and correction of Partition coefficient $K_{oc}$**

(Karickhoff *et al.*, 1979; Bochting *et al.*, 1993)

$$K_{oc} = K_{ow} \cdot f_{nd}$$

$f_{nd}$  is the non-dissociated fraction, calculated from  $1/[10^{(pH-pK_a)}+1]$ .

$K_a$  is the equilibrium constant for the acid dissociation reaction.

The pH is given an average value (8).

For each of the grid cells defined in the environment input-panel, common mass balance equations for the compounds in the watercolumn and the sediment layer have been defined in the steady state version of DELWAQ-2D. A description of the basic set of formulae used in DELWAQ-2D is presented in the following sections (5.4.1 to 5.4.3).

Default environmental property data are indicated in Annex IV for the compounds in the default model-database, and were used in the various model runs described in the validation chapter. It should be noted that these values are recommended generic values, based on the current information provided by participants in the CEPE AFWG. Some properties may be dependent on environmental conditions (e.g. photolysis, hydrolysis). It is the responsibility of the user or risk-assessor to replace the default values and to select the most adequate parameter values.

##### **5.4.1 Chemical fate in the water column**

The mass balance equation for the water column of a compartment in a steady state is described with:

load + inflow - outflow - settling - volatilisation - decomposition = 0

$$L + Q_i.C_i - Q_o.C_t - F_s.P.f_{df}.C_w - r_v.f_{df}.C_w.V_w - r_w.C_w.V_w = 0 \quad [1]$$

with:

$$F_s = v_s.S_s.f_c.A_w \text{ for organic compounds} \quad [1a]$$

$$F_s = v_s.S_s.A_w \text{ for metals} \quad [1b]$$

in which:

$A_w$	= surface area of the compartment ( $m^2$ )
$C_t$	= total concentration in the water column ( $g.m^{-3}$ )
$f_{df}$	= freely dissolved fraction (-)
$f_c$	= for organic compounds : fraction organic carbon in suspended solids (-)
$F_s$	= settling load of suspended organic carbon ( $g \text{ OC.day}^{-1}$ )
$L$	= load of compound ( $g.day^{-1}$ )
$P$	= for organic compounds : Koc partition coefficient ( $10^{-6} \text{ l.kg}^{-1} \text{ OC}$ ) = for metals: Kd partition coefficient ( $\text{l.kg}^{-1}$ )
$Q_o$	= total outgoing flow rate ( $m^3.day^{-1}$ )
$Q_i$	= total ingoing flow rate ( $m^3.day^{-1}$ )
$C_i$	= total concentration at ingoing flow ( $g.m^{-3}$ )
$r_v$	= volatilisation rate ( $day^{-1}$ )
$r_w$	= overall first order decomposition rate in the water column ( $day^{-1}$ )
$S_s$	= concentration of suspended solids ( $g.m^{-3}$ )
$v_s$	= net settling velocity ( $m.day^{-1}$ )
$V_w$	= water volume ( $m^3$ )

Some parameters in equation [1] are aggregate parameters, which are quantified from other simple algebraic relations. Load  $L$  represents the emissions of the antifoulant discharges (specified in the emission input-panel). The emissions are assumed to take place evenly distributed in the grid cells along the rear end of the harbour or marina. In the shipping lane, this is assumed to take place in the central row of grid cells. The outgoing flow rate  $Q_o$  may be the sum of several flow rates going to as many downstream or adjacent compartments (grid cells).

The detritus settling resulting from phytoplankton mortality is taken into account as part of the suspended matter settling, expressed in organic carbon units (OC).

The dissolved fraction  $f_{df}$  is derived from the partitioning of a substance between water, dissolved organic matter, (organic) suspended matter. Not only dissolved fractions, but also particulate fractions are deduced using partition coefficients (see following section).

The overall first order decomposition rate in the water column  $r_w$  is derived from the rate constants specified for photolysis, hydrolysis and biodegradation, if all of these contributions are separately known. The user needs to provide reliable data. Hydrolysis and biodegradation may be assumed to take place evenly distributed over the whole water column. It should be noted that most degradation rates can be scenario-specific. As an example, the hydrolysis rate constant of dichlofluanid is known to increase with pH and temperature (Bayer AG, 2002a)

The contribution of photolysis is only relevant during day time at water depths with sufficient transmittance. The rate of photolysis is dependent upon many factors, such as time of year, latitude, depth, atmospheric conditions and several factors which effect the light transmission characteristics of the water body (Mill, 2000). Proper handling of photolysis can only be executed in 3D models. In the WAQ module of Delft3D (WL, 1996), libraries and protocols are provided. EXAMS (Burns, 2000) also has modules proper handling of photolysis. Extrapolation of laboratory derived photolysis rate constants needs to be done with care. The user should provide reliable corrections for day/light regime and the water layers in which photolysis constitutes a significant contribution. The current version of MAM-PEC is not capable of calculating the proper photolysis rate for each environment scenario, and has a default value of 0 (except for zinc pyriithione). If applicable, appropriate photolysis rates for local conditions must therefore be determined offline and substituted for the default value in MAM-PEC. Two approaches can be taken:

- 1) Various available software packages, capable of 3D modelling may be used, such as EXAMS, DELFT 3D or alternatively GCSOLAR, from U.S. EPA ( <http://www.epa.gov/ceampubl/swater/index.htm> )
- 2) If a measured photolysis rate is available at a known surface solar irradiance, then the average photolysis rate ( $k_{D2-D0}$  in  $\text{day}^{-1}$ ) over the depth of a shallow water body from the surface ( $D0$ ) to depth  $D2$  under those conditions may be calculated, according to Neely et al. (1985) , using the equation:

$$k_{D2D0} = k_{D0} ( 1 - e^{-(K_T * D2)} ) / (K_T * D2)$$

where  $K_T$  is the total optical diffuse attenuation coefficient ( $\text{m}^{-1}$ ) for the water body and  $k_{D0}$  ( $\text{day}^{-1}$ ) is the surface photolysis rate.  $K_T$  should be known for relevant wavelengths. For instance for application to zinc pyriithione,  $K_T$  should be measured in the region of 310-350 nm. Since photolysis rate is directly proportional to solar irradiance, the photolysis rate at a different surface irradiance value can be easily calculated. The averaged rate constant assumes complete vertical mixing. In order to be relevant to risk assessments for antifouling applications, and depending on the dynamics of emission patterns and chemical fate processes, photolysis rates for antifoulants form pleasure crafts should be calculated for the local boating season only.

The volatilisation rate  $r_v$  is a function of substance and compartment specific coefficients:

$$R_v = (h \cdot (1/k_l + 1/(H_{a1} \cdot k_g)))^{-1} \quad [2]$$

$$H_{a1} = H_{a2} \cdot (R \cdot (T_a + 273.15))^{-1} \quad [3]$$

in which:

$h$	= depth of water column (m)
$H_{a1}$	= dimensionless Henry's constant at average temp. ((mol.m <sup>-3</sup> ). (mol.m <sup>-3</sup> ) <sup>-1</sup> )
$H_{a2}$	= Henry's constant at average ambient temperature (Pa.m <sup>3</sup> .mol <sup>-1</sup> )
$k_g$	= mass transfer coefficient in the gas film (m.d <sup>-1</sup> ), compartment specific
$k_l$	= mass transfer coefficient in the liquid film (m.d <sup>-1</sup> ), compartment specific
$R$	= gas constant (8.3 Pa.m <sup>3</sup> .mol <sup>-1</sup> .°K <sup>-1</sup> )
$T_a$	= average ambient temperature (10 °C)

The decomposition rate  $r_w$  is substance and compartment specific. The parameters  $r_w$  and  $H_{a2}$  are temperature dependent, approximately according to:

$$\text{par}_T = \text{par}_{20} \cdot T_c^{(T_a-20)} \quad [4]$$

in which:

$\text{par}_{20}$	= $H$ or $r_w$ at a temperature of 20 °C
$T_c$	= temperature coefficient (approximately 1.07)

#### 5.4.2 The sediment layer

In order to determine the contaminant concentration in the upper sediment layer, a fully (homogeneous) mixed sediment layer is defined with a density  $\rho$  and a thickness of  $\delta$ . Assuming that the sediment influx towards this sediment layer equals the outgoing flux of the sediment layer, the mass balance equation for the homogeneous mixed upper sediment layer can be described by:

$$\frac{dC_m}{dt} = \frac{F}{rd} \cdot C_p - C_m \left( \frac{F}{rd} + k \right) \quad [5]$$



in which:

$F$	= sedimentation flux of suspended matter ( $\text{g} \cdot \text{m}^{-2} \text{d}^{-1}$ ) = $v_s \cdot S_s$
$C_m$	= contaminant concentration in upper sediment layer (mg/kg)
$C_p$	= contaminant concentration in suspended matter (mg/kg)
$\rho$	= dry density of sediment in upper layer ( $\text{g} \cdot \text{m}^{-3}$ )
$k$	= decomposition rate of contaminant in sediment ( $\text{d}^{-1}$ )
$\delta$	= thickness of homogeneous mixed upper layer (m)

In case of steady-state ( $dC_m/dt = 0$ ) and a decomposition rate of zero ( $k=0$ ), the concentration adsorbed to suspended matter equals the contaminant concentration in the sediment. This approach was taken in the first version of the Mam-Pec model (v 1.2). Solving the above differential for heavy metals analytically, assuming an initial sediment concentration of zero and assuming that the  $C_p$  is constant over the time, yields:

$$C_m(t) = \frac{\frac{F}{r \cdot d}}{\frac{F}{r \cdot d} + k} \cdot C_p (1 - e^{-\left(\frac{F}{r \cdot d} + k\right)t}) \quad [6]$$

The density of the sediment depends on the characteristic of the sediment layer. For a sandy sediment layer a value of  $1500 \text{ kg/m}^3$  and for a muddy layer a value of  $500 \text{ kg/m}^3$  is appropriate. The sedimentation flux  $F$  is determined by the user defined sedimentation velocity and the suspended matter concentration in the water phase. In order to get a first rough estimate of the net sedimentation velocity, the yearly amount of fine dredged material in the harbour can be divided by the averaged concentration of suspended material in the harbour. Suppose a dredged amount of fine material of 500 kton dry weight per year over an area of  $50 \text{ km}^2$ . An averaged concentration of  $50 \text{ g/m}^3$  results in a net sedimentation velocity of approximately  $0.5 \text{ m/d}$ .

The thickness of the homogeneous mixed upper sediment layer depends on the local physical conditions, human activities (i.e. dredging) and the biological activity. Appropriate values in estuarine systems are in the range of 0.1 to 0.5 meter. The applied thickness determined as an average value on a yearly basis, as the time-scale of the sediment processes is in the order of decades.

#### 5.4.3 Partitioning and exposure - mean equilibrium concentrations

Partitioning among the dissolved and particulate phases affects the loss and distribution of a substance as well as the exposure of organisms to this substance. Partitioning is

formulated according to the equilibrium concept of partition coefficients. The total concentration of an organic micropollutant is the sum of three contributions:

$$C_t = (f_{poc} + f_{doc} + f_{df}) \cdot C_t \quad [7]$$

in which:

$$\begin{aligned} C_t &= \text{total concentration (g.m}^{-3}\text{)} \\ f_{df} &= \text{freely dissolved fraction (-)} \\ f_{doc} &= \text{fraction adsorbed to dissolved organic matter (-)} \\ f_{poc} &= \text{fraction adsorbed to the organic part of (suspended) matter (-)} \end{aligned}$$

All organic matter is expressed in amounts of carbon. The fractions are derived from a partition coefficient defined according to:

$$P = C_p / (f_{df} \cdot C_t) \quad [8]$$

in which:

$$\begin{aligned} C_p &= \text{particulate concentration (g.g}^{-1} \text{ OC)} \\ P &= \text{partition coefficient (m}^3 \cdot \text{g}^{-1} \text{ OC} = 10^{-6} \text{ l.kg}^{-1} \text{ OC)} \end{aligned}$$

The partition coefficient (P) is usually available as  $K_{oc}$  ( $\text{l.kg}^{-1}$ ), the conversion of which into P requires a multiplier of  $10^{-6}$ . Linear relations are available to estimate  $K_{oc}$  on the basis of the octanol-water partition coefficient ( $K_{ow}$ ;  $\text{l.kg}^{-1}$ ).

The fractions follow from:

$$f_{df} = 1 / (1 + P \cdot C_{toc}) \quad [9]$$

$$f_{poc} = (1 - f_{df}) \cdot C_{poc} / C_{toc} \quad [10]$$

$$f_{doc} = (1 - f_{df}) \cdot X_{doc} \cdot C_{doc} / C_{toc} \quad [11]$$

$$C_{poc} = f_{oc} \cdot S_s \quad [12]$$

$$C_{toc} = C_{poc} + X_{doc} \cdot C_{doc} \quad [13]$$

in which:

$$\begin{aligned} C_{doc} &= \text{dissolved organic carbon concentration (g OC.m}^{-3}\text{)} \\ C_{toc} &= \text{total organic carbon concentration (g OC.m}^{-3}\text{)} \\ f_{oc} &= \text{fraction organic carbon in suspended solids} \\ S_s &= \text{(suspended) sediment concentration (g.m}^{-3}\text{)} \\ X_{doc} &= \text{sorption efficiency relative to particulate organic carbon (-)} \end{aligned}$$

Combining the fractions with the total concentration yields the individual probable exposure concentrations (PEC) in water and particulate matter. Similar formulations can be used for heavy metals, but then sorption is considered relative to the total mass of (suspended) sediment instead of its organic part. Options to calculate concentrations in other biota (fish, molluscs, crustaceans) are present in the DELWA-2D, but have been hidden in the MAM-PEC model.

## 5.5 Emission scenarios

The emission scenario input screen of the MAM-PEC model consists of the following elements:

- input block for total emission ( $E_{tot}$ ) calculated by MAM-PEC (based on specified settings) or to provided by the user if such a figure is known from a specific emission inventory study;
- input block for shipping characteristics. The user can define 10 categories (length categories is used as default) of ships and provide for each of these categories: the estimated surface area ( $A_i$ ) per ship for each of these categories, the number of ships present in the harbour at berth ( $N_{ib}$ ) or moving in the harbour ( $N_{im}$ ), shipping lane/open sea sector, the application factor ( $Ap_i$  %) of the antifouling product applied;
- input block for leaching rate for ships at berth ( $LR_b$ ) or moving ( $LR_m$ ).

Based on the data provided for the shipping characteristics and the leaching rate the MAM-PEC model calculates the total emission with the formula indicated below.

$$E_{tot} = \text{Sum}_{\text{cat1-10 at berth}} (A_i * N_{ib} * Ap_i * LR_b) + \text{Sum}_{\text{cat1-10 moving}} (A_i * N_{im} * Ap_i * LR_m)$$

The total number of ships present in the harbour should be expressed as present at any time of the day. For the commercial harbour and estuarine harbour an average residence time of 3 days was used for ships at berth, and a harbour manoeuvring time for arrival and depart was taken as 3 hours.  $N_{ib}$  and  $N_{im}$  were derived from the total cumulative annual port statistics:

$$N_{ib} = N_{iby} * 3 / 365 \quad N_{im} = N_{imy} * 0.125 / 365$$

in which:

$N_{iby}$  = total number of port visits per year in specific length category.

$N_{imy}$  = total number of ship movements per year in the specific length class in the harbour.

The total number of ship movements includes not only arrivals and departs of ships visiting the harbour, but also transits of ships sailing to upstream locations. The length categories of these ships usually are not known, but are attributed to the smallest length category. The settings for various emission scenarios have been indicated in Table 5.2.

For the shipping lane and the open sea the number of ships present in the area or shipping lane should be provided as number present at any time of the day, as presented in

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Chapter 2. For the shipping lane the eastern section of the main shipping lane along the Dutch coast was taken with an average density of 41 ships per 1000 km<sup>2</sup>. For the open Sea one of the Northern sections of the Dutch Continental Sector was taken with an average density of 1 ship per 1000 km<sup>2</sup>. The length distribution and surfaces of the default commercial harbour were used.

The settings for the marina have been indicated in Table 3.4, and were derived from the Mediterranean marine in Golfe Juan from the paper of Baur and Jacobson (1996). The number of moving ships has not been indicated, as manoeuvring time in marinas is expected to be negligible to the time at berth.

The user has the option to modify the categories and surface areas per ship, if such data are known from other studies. A fixed module to calculate the surface area with one of the approaches described in Chapter 3 was not included in the model, as the estimation of the surface area constitutes a source of significant variation. For comparative purposes, the values provided in the default emission scenarios, which cannot be edited by the user (Table 5.2) were considered suitable. The average surface areas were calculated according the method described by Williamson and Jacobson (1996).

*Table 5.2 Shipping related settings of default emission scenarios.*

Scenario	Category length class in m	Surface Area average m <sup>2</sup> per ship	N <sub>at berth</sub> at any time of the day	N <sub>moving</sub> at any time of the day
Default Commercial Harbour	50-100	450	57	8.75
	100-150	3061	25.5	2.15
	150-200	5999	24.5	2.05
	200-250	9917	5.5	0.5
	250-300	14814	7.5	0.6
	300-350	22645	1.5	0.1
Default Estuarine Harbour	50-100	450	11	1.8
	100-150	3061	5	0.4
	150-200	5999	5	0.4
	200-250	9917	1	0.1
	250-300	14814	2	0.1
Default Shipping Lane	50-100	450		3.9
	100-150	3061		1.7
	150-200	5999		1.6
	200-250	9917		0.4
	250-300	14814		0.5
	300-350	22645		0.1
Open Sea	50-100	450		0.095
	100-150	3061		0.04
	150-200	5999		0.04
	200-250	9917		0.01
	250-300	14814		0.01
	300-350	22645		0.002
Marina	1-50	22.5	299	

The application factor is set in the default scenarios at 100 %. The user may edit this value for user-defined emission scenarios.

For the leaching rates the values indicated in Chapter 3 were used, with no distinction between ships moving or at berth.

## 5.6 Background concentrations

After finishing the input screens for environment, compounds and emission scenario, the user may specify a background concentration. Especially in the shipping lane and open sea scenarios the mixing with water masses with a specific background concentration has a significant influence on the calculations. In the default scenarios this value was set to zero.

## 5.7 Calculation Results

After finishing all the input screens the calculations are started. The model run is assigned automatically a unique name, based on the environmental scenario, the compound and emission scenario selected. Together with the provided background concentration the specific settings are stored by the user interface in the central database.

For each of the grid cells the expected steady state concentrations are being calculated and stored in temporary files. This results in a distribution of concentrations in the specified environment (see the example provided in Figure 5.3).

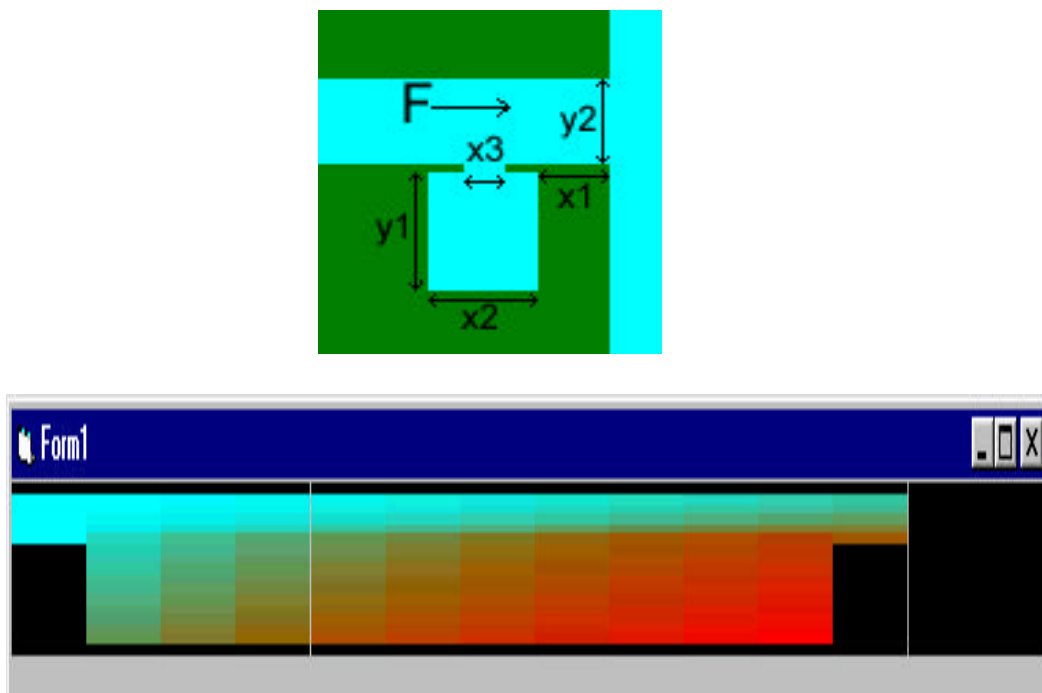


Figure 5.3 Plot of relative concentration distribution in a commercial harbour scenario. (Presentation option not supported in model).

Average, median, minimum, 95-percentile, and maximum concentrations are being calculated for the harbour section for the dissolved concentration ( $\mu\text{g/L}$  including both the

freely dissolved and the DOC-bound fraction), the total aqueous concentration ( $\mu\text{g/L}$  including fraction bound to particulate matter), the concentration on particulate matter, and the sediment ( $\mu\text{g/g}$  organic carbon dry wt basis). As sediment mixing processes are slow, and attaining steady state may take years to decades, the model calculates sediment concentrations for different time periods (1-2-5-10 year). For most organic compounds steady state conditions are reached within this time frame. However, for some compounds with slow (TBT) or absent (total copper) degradation in sediment, this may involve longer time periods.

These values are added to the database and presented in the results screen. An option to provide a graph of the spatial distribution (as in figure 5.3) is not supported in the current version

In order to allow easy comparisons with monitoring data, the SPM and sediment concentrations are presented in the results screen on a dry weight basis. Conversions to SPM or sediment concentrations on an organic carbon basis need to be done manually (based on the POC and foc settings provided in the environment screen). However, advanced users may access the database of the model, as sediment and SPM concentrations in the model and database are handled on organic carbon basis (see note for advanced users in the version 1.4 help-files of the model).

From the results screen a print-file can be displayed, containing detailed scenario settings, results of the calculations, date and model version number, press the button Print. The shown text can be send to the printer or an \*.txt or \*.rtf file. The \*.txt file can be imported in programs like Excel (suggestion : select ":" as the field separator).

Results from previous model-runs can be easily accessed using a list box in the results screen.

The statistics provided in the results-screen are spatially averaged values. For the harbour and marina scenarios these are calculated for the port section. For the adjacent river or coastal water sections lower values are predicted, but not presented. In the helpfiles to the model an explanation is given for advance users how to examine predicted values for individual grid cells (both in port section and adjacent waters. In the shipping lane and open sea scenarios the statistics are given for the total area. It should be noted that maximum values only occur directly below the emissions, which are situated in the rear end of the harbour (and central line in the off coast scenarios). It should further be noted that the statistics are not comparable to results from probabilistic models, in which the variability of all model parameters is reflected in the final statistics. Inclusion of probabilistic approaches and an interactive sensitivity-analysis module is considered as an option for future versions of Mam-Pec. It is the responsibility of the user or risk assessor to determine which statistics (minimum, median, average, 95 percentile, maximum) need to be used.

## 5.8 Copper speciation module

For the results screen of copper an additional module has been added, calculating the expected speciation and free  $\text{Cu}^{2+}$  concentrations in the water column, according to the 3-ligand model proposed in the recent review and modelling study on Cu speciation in the marine environment by Karman *et al.* (1998). In this study it was demonstrated that the

free  $\text{Cu}^{2+}$  concentration, strongly depended on the local concentrations of particulate matter, modelled ligands, pH, salinity and the total copper concentrations. For open sea and coastal waters most of copper is bound to two sets of operationally defined organic ligands: Li (1) and Li(2). In estuarine waters and harbours a third organic ligand, Li(3) with medium high stability constants is assumed.

Reactions, stability constants, and assumed concentrations of the three main ligands for the different environmental scenarios were taken similar as in the study of Karman *et al.* (1998) and included in a calculation module, in which the set of equations is solved with an iterative optimisation procedure. The basic settings are indicated in Table 5.3 and are based on settings provided in the environment input-screen, predicted total Cu concentrations by the MAM-PEC model and some default values according to Karman *et al.* (1998). The predicted free  $\text{Cu}^{2+}$  ion concentration ranges with the module in MAM-PEC were similar as the values predicted by the Titrator programme in Karman *et al.* (1998). Typical values for the fraction of free  $\text{Cu}^{2+}$  ranged from  $< 0.1 - 2\%$  of the total Cu concentrations.

It should be noted that currently available data on stability constants (included in databases of most speciation computer models) is limited mainly to inorganic complexes. The identification and stability constants of most organic ligand complexes have hardly been determined. Although the proposed 3 ligand model has not yet been properly validated, it is currently accepted by many experts (Donat & Bruland, 1995; Gordon *et al.*, 1996; Donat *et al.*, 1997; Miller & Bruland, 1997).

Table 5.3 Settings of Cu-speciation module included in results section of model. Overview of complexation reactions included, stability constants (K) and default concentrations (in nM/L) provided.

Reactions included:	Stability constant K		Concentration nM
$\text{Cu}^{++} + \text{Li}(1)^{-} = \text{CuLi}(1)$	1E+12	CuT	**
$\text{Cu}^{++} + \text{Li}(2)^{-} = \text{CuLi}(2)$	1E+08	Li(1)T	***
$\text{Cu}^{++} + \text{CO}_3^{--} = \text{CuCO}_3$	501187.2	Li(2)T	***
$\text{Cu}^{++} + \text{OH}^{-} = \text{CuOH}^{-}$	1000000	H+	*
$\text{H}^{+} + \text{CO}_3^{--} = \text{HCO}_3^{-}$	1E+10	$\text{CO}_3^{--}$	0.00021
$\text{H}^{+} + \text{Li}(1)^{-} = \text{HLi}(1)^{-}$	1E+08	OH-	2.95E-06
$\text{H}^{+} + \text{HCO}_3^{-} = \text{H}_2\text{CO}_3$	2300000	pH	*
$\text{H}^{+} + \text{OH}^{-} = \text{H}_2\text{O}$	13.73	Mg++	0.0436
$\text{Mg}^{+} + \text{CO}_3 = \text{MgCO}_3$	71.2853	Ca++	0.00851
$\text{Ca}^{+} + \text{CO}_3 = \text{CaCO}_3$	135.8313	Cl-	*
$\text{Cu}^{++} + \text{Cl}^{-} = \text{CuCl}$	0.467735	Li(3)T	***
$\text{Cu}^{++} + \text{Li}(3)^{-} = \text{CuLi}(3)$	1000000		
$\text{H}^{+} + \text{Li}(2)^{-} = \text{HLi}(2)$	1E+10		
$\text{H}^{+} + \text{Li}(3)^{-} = \text{HLi}(3) :$	1E+6		
$\text{Cu}^{++} + \text{SO}_4^{--} = \text{CuSO}_4$	1E+1.27		

\* Provided in environment input screen; \*\* Total Cu concentration from model calculation results; \*\*\* Total concentrations of Ligands 1,2 and 3 default ranges provided for open sea, coastal waters and estuaries and harbours according to Karman *et al.* (1998): 20 - 110 nM for Li(1)T; 75 - 500 nM for Li(2)T and 5000 - 50,000 nM for Li(3)T.

Although it is acknowledged, that the binding of copper bound to different sediment phases is expected to result in a low bioavailability (Campbell *et al.*, 1988), and that a total sediment copper concentration (as calculated by the model) has a limited significance for the estimation of environmental risks, no attempts were made to include a sediment speciation module.

Especially the binding to relatively insoluble sulphides is expected to have a major impact on the bioavailability of sediment bound copper. Since 1990 much attention has been given to the importance of Acid Volatile Sulphide (AVS) as one of the major parameters with respect to the prediction of toxic effects of metals in anaerobic sediments (Ankley *et al.*, 1993). AVS is an operationally defined parameter and is a measure of the available amount of sulphide in sediments. The general concept is that due to the very low solubility of metal sulphide precipitates, simultaneously extracted metals (SEM) will not be available for uptake by organisms in the presence of excess available sulphide. In the Netherlands, van den Hoop *et al.* (1997), determined the ratio of simultaneously extracted metals (SEM) to AVS in marine and freshwater habitats (21 sites). AVS was detected in 95% of the sediments tested (19 of the 21 sites) and the corresponding SEM/AVS ratio at the 19 sites was found to be less than one, indicating a low bioavailability. Sediments can be a major source for copper-complexing ligands. Skrabel *et al.* (1997) demonstrated in study in Chesapeake Bay, that the fluxes of copper-complexing ligands from sediments ( $300\text{-}1200 \text{ nmol m}^{-2} \text{ d}^{-1}$ ) exceeded the fluxes of copper by 3-40 fold, suggesting that any copper fluxing from the sediments is likely to be organically



complexed. This could therefore be a further factor in the bioavailability of copper in both sediments and sediment-pore water.

## 6. Validation of model predictions

Model predicted concentrations were compared to results from monitoring studies. Automated searches in available on-line literature databases (Current Contents, Chemical Abstracts, Biosis, Toxline covering the period 1980-1998) on monitoring studies of antifouling products revealed a wealth of data on mainly TBT and to a lesser extent Cu, Irgarol and some other products.

Useful reviews on TBT were found in Fent (1996), Evers *et al.* (1995), Lange (1996, 1997) and Karlsson (1997). Many of the Cu directed studies could not be used without a prior evaluation of natural background concentrations and contributions from other sources. Such an evaluation has recently been conducted by Hall and Anderson (1997). The same holds for some studies on Diuron, most of which are directed to agricultural or riverine discharges. For many of the new products, reliable analytical methods (based on GC-MS or LC-MS) have only recently been developed and not yet applied on a large scale (Thomas, 1998; Steen *et al.*, 1997 )

Monitoring data derived from review studies have presented for organotins (Table 6.1) and Irgarol (Table 6.2). For copper we refer to the comprehensive review of Hall and Anderson (1997). The overall reported ranges for the various compounds have been summarised in Table 6.3 for harbours, marinas, estuaries and open sea. The available data confirm hypothesised distribution patterns, with the highest concentrations in harbours and marinas and decreasing gradients towards open sea locations.

The predictions from model runs with the provided default scenarios are indicated in Table 6.4. Basic settings of the model runs have been listed in Appendices IV, V, VI and VII. As can be seen the model predicted PECs are reasonably in the range of values reported from monitoring studies. In Table 6.5 a comparison is made with predictions from the simple marina box-models.

*Table 6.1 Measured TBT (in ng/L) in European harbours, estuaries and open sea.*

Harbour, period	Coastal area	Mouth	Estuary	Harbour	Open Sea
Bremerhaven (1990-1993)	5 - 10	15 - 30	20 - 35	200 - 350	
Genoa (1990-1992)	<5 - 10			80 - 150	
Rotterdam (1990-1993)	5 - 10	10 - 15	20 - 25	35 - 40	
Milford Haven (1990-1993)	3 - 3	4 - 6		4 - 9	
North Sea, German Bight					1
North Sea, central area					0.01
British Channel					0.5

Source: Lange (1996).

Table 6.2 Concentrations of Irgarol 1051 (ng/L) in the marine environment.

Location	Date	Marinas	Ports	Estuarine	Coastal areas	Ref.
Côte d'Azur, Fr.	June 1992	110-1700	<5-280	n.s.	n.d.	2
Southern England	July- Sept. 93	52-500	9-14	4-18	<2-11	3
W. Coast Sweden	May-Sept. 94	30-400	n.s.	n.s.	n.d.	1
Eastern England	April 95	682	n.s.	1-39	n.m.	4
Eastern England	June 95	536	n.s.	<1-10	n.m.	4
Eastern England	Sept. 95	169	n.s.	4-10	n.m.	4
Lake Geneva	Aug 94- Apr 95	10-140	n.s.	n.s.	n.s.	5
Western Scheldt	Mar 96-Aug 96	5-35 <sup>a</sup>	n.s.	1-10	n.s.	8
Stockholm	Apr-Oct 96	6-130	n.s.	n.s.	<4-5	7
Delta Ebro	Apr 1996- Feb 97	300	n.s.	n.s.	7-90	6

n.s.: not sampled ; n.m.: not measured ; n.d.: not detected. <sup>a</sup>) River Scheldt and Canal from Gent to Terneuzen.

Source: 1. B. Dahl and H. Blanck (1996). 2. J.W. Readman *et al.* (1993); 3. M.A. Gough *et al.* (1994); 4. J. L. Zhou *et al.* (1996) ; 5. S. Tóth *et al.* (1996); 6. I. Ferrer *et al.* (1997); 7. Haglund and Petterson S. Lord *et al.* (submitted); 8. R.J.C.A. Steen *et al.* (1997).

Table 6.3 Summary of reported values (ng/L) from monitoring studies.

	Marinas	Ports	Estuaries	Coast/Sea	Ref.
TBT		40-350	20-35	.01-1	1)
Irgarol	30-1700	9-280	<1-39	<0.1-11	2)
Copper		260-1600	280-5480	69-5560	3)

Refs: 1) Lange (1996); 2) Steen (1998); 3) Hall and Anderson (1998).

Table 6.4 Results of validation runs with the MAM-PEC Model (version 1.4). Predicted environmental concentrations (PECs) in the default scenarios compared to literature data.

Scenario	Leaching rate µg/cm <sup>2</sup> /day	Appl. factor %	PEC (ng/L)			Lit. values*
			average	min.	max	
<b>TBT</b>						
Default commercial harbour	4	100	248	5	739	20-350
Default estuarine harbour	4	100	104	4	297	20-350
Default marina	4	100	161	35	233	40-350
Default shipping lane	4	100	0.1	<0.01	0.7	0.01-1
<b>Irgarol</b>						
Default marina	2.5	100	101	22	147	30-1700
Poorly flushed marina	2.5	100	1140	514	1610	30-1700
<b>Copper</b>						
Default commercial harbour	50	100	3211	67	9765	260-1600
Default marina	50	100	1992	434	2896	

Settings of environment, compounds and emission scenario are indicated in Appendices IV, V, VI and VII. \* Literature values derived from Table 6.3.

Table 6.5 Comparison of predictions using Mam-Pec (version 1.2) with results from other antifoulant modelling studies (in ug/L)\*

Compound, scenario	Predicted concentration mean (min-max range)	Reported values	Source
<b>TBT</b>			
Dutch Marina-1	10 (3 - 15)	8.1	J&L (1994)
Dutch Marina-2	0.12 (.06 - .17)	0.15	B&J (1997)
Golfe Juan Marine	0.09 (.05 - .17)	0.11	B&J (1997)
Antibes Marina	0.08 (.04 - .15)	0.09	B&J (1997)
<b>Sea-Nine</b>			
Dutch Marina	0.034 (.01 - .06)	0.026	B&J (1997)
Golfe Juan Marina	0.024 (.008 - .078)	0.019	B&J (1997)
Antibes Marina	0.021 (.006 - .08)	0.016	B&J (1997)

\* settings as in papers cited: Johnson and Luttkik (1994); Bauer and Jacobson (1997)

### Rotterdam Case Study

The Mam-Pec model (version 1.2) was used in a study to predict antifoulant concentrations in the Port of Rotterdam (Van Hattum and Baart, 2001). The complex geometry and hydrography of the port of Rotterdam was approached with two different scenarios. In the first scenario the geometry of the Rotterdam port area was conceptualised as a rectangular area (2 x 20 km; 4000 ha; depth 20 m), with a 5 km wide open front to the river in order to mimic a harbour segment with an average water exchange of 32% per tidal period. A second scenario, with a 10 km wide open front to the river was chosen to represent harbour segments with a water exchange of 65% per tidal period. Settings and dimensions have been documented in Van Hattum and Baart (2001). Emissions of TBT in the Port of Rotterdam were estimated using 1998 shipping data and ranged from 4 - 13 t/y (lower estimate based on leaching rate of 1 µg/cm<sup>2</sup>/day for non-moving ships). The emissions of TBT in the port of Rotterdam rank among the highest in the world. The majority of the TBT emissions are caused by the larger ship classes (> 100 m); the relatively large number of small ships (n = 13636 in 1998; 46% of total nr of ships) contributes to only 6 % of the total TBT emissions.

The range of sediment TBT concentrations predicted with the Mam-Pec model (0.01 – 2.8 mg/kg; see Table 6.6 and 6.7) for harbour segments with different rate of water exchange per tidal period (32% and 65%) coincides with gradients reported from monitoring studies in the Nieuwe Waterweg (Stronkhorst, 1996), as well as ranges reported for other international harbours. Median and average values (0.07 – 1.9) are comparable to harbours in eastern section of the Rotterdam port area and to some harbours in the western section of the port of Rotterdam, not exchanging directly with the Nieuwe Waterweg.

*Table 6.6 Predicted concentrations of TBT for the Port of Rotterdam for segments with an average water exchange of 32% per tidal period*

	Dissolved µg/L	Total* µg/L	Sediment mg/kg Org-C	Sediment** mg/kg dry weight
Average	0.82	0.85	33	1.6
Median	0.95	0.99	38	1.9
Minimum	0.006	0.007	28	0.01
P <sub>95</sub>	1.40	1.45	56	2.8
Maximum	1.40	1.46	56	2.8

\* based on concentration of suspended matter of 35 mg/L with 3% Org-C; \*\* sediment with 5% Org-C

*Table 6.7 Predicted concentrations of TBT for the Port of Rotterdam for segments with an average water exchange of 65% per tidal period*

	Dissolved µg/L	Total* µg/L	Sediment mg/kg Org-C	Sediment** mg/kg dry weight
Average	0.39	0.41	16	0.7
Median	0.04	0.04	1.4	0.07
Minimum	0.007	0.007	0.3	0.01
P <sub>95</sub>	1.2	1.2	46	2.3
Maximum	1.2	1.2	46	2.2

\* based on concentration of suspended matter of 35 mg/L with 3% Org-C; \*\* sediment with 5% Org-C

## Application to European marinas

In the recently finished ACE project (Assessment of Antifouling Agents in Coastal Environments) supported by the MAST-III Program of the Commission of the European Community ACE (contract MAS3-CT98-0178) monitoring surveys were conducted in several European countries on exposure levels of common antifouling agents in marinas (Readman, 2002). The Mam-Pec model (version 1.4) was used to predict exposure concentrations of Irgarol based on harbour geometry, local hydrodynamics and shipping characteristics. Predicted values (Van Hattum et al., in preparation) were in reasonable agreement (order of magnitude matching) with ranges of observed concentrations (see figure 6.1). Model settings for the environment and emission sections are listed in Annex-8. For the compound properties we used the default values for Irgarol.

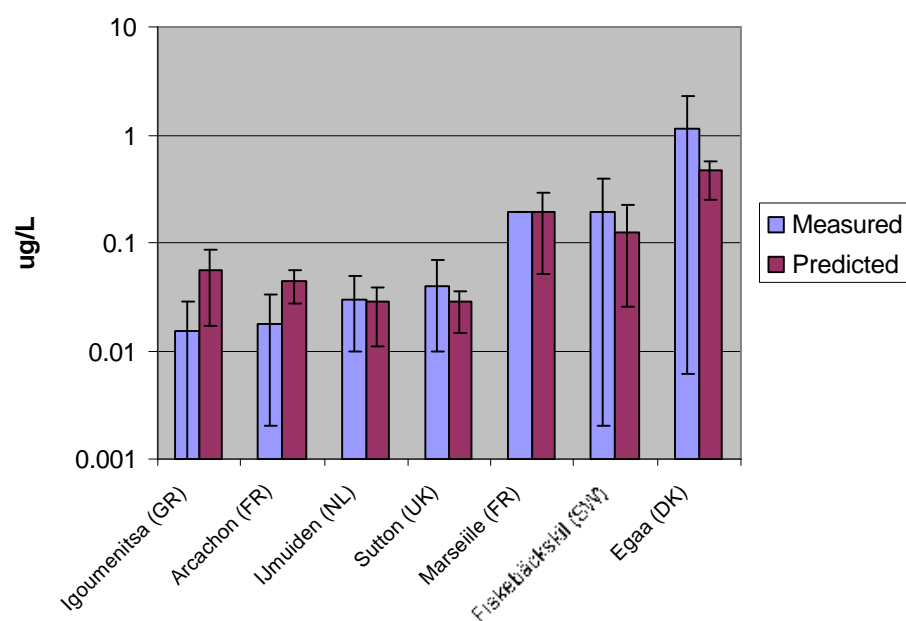


Figure: 6.1 Comparison of measured concentrations of Irgarol ( $\mu\text{g/L}$ ; average values) in European marinas and predictions based on the Mam-Pec model. Error bars indicate the min-max range of predictions and measurements inside the marinas Source: Readman (2002).



## 7. Conclusions

The estimation of realistic Predicted Environmental Concentrations (PECs) is essential for predictive environmental risk assessment. Many new antifouling products are expected to be brought on the market in the coming decade. Large uncertainties are involved in the estimation of emissions of antifouling biocides, due to assumptions made with respect to leaching behaviour and shipping characteristics. The chemical fate of antifouling products in the marine environment is determined to a large extent by complex and interacting hydrodynamic processes. Therefore, there is a need for a standardised and widely applicable modelling tool for the assessment of PECs of antifouling biocides in the marine environment.

An evaluation of existing models revealed that current assessment models are largely unsuitable to cope with complex emission patterns and marine hydrodynamics, which both have a significant impact on the chemical fate of antifouling products. Although some models may be suitable for a specific environment, none of the currently available models was suitable for all the prototype environments specified.

Against this background a generic prototype-model (MAM-PEC) was designed, which generates predicted environmental concentrations for five fixed default marine environments (open sea, shipping lane, estuary, commercial harbour, yachting marina). Used defined environments can be adapted to local situations and added. Settings for the specific environments, compounds and emission scenarios are entered and edited via input-screens, which can easily be accessed via central User Interface (UI), which guides the user during the modelling sessions. The UI further gives further access to calculation results and explanatory helpfiles and maintains a database in which settings and calculation results are stored. The first version of the model (version 1.2) was released in 1999. Based on evaluations and experiences of users a new release (version 1.4) was issued in August 2002.

The model takes into account emission factors (e.g., leaching rates, shipping intensities, residence times, ship hull underwater surface areas), compound-related properties and processes (e.g.,  $K_d$ ,  $K_{ow}$ ,  $K_{oc}$ , volatilisation, speciation, hydrolysis, photolysis, bacterial degradation), and properties and processes related to the specific environment (e.g., currents, tides, salinity, suspended matter load). A special module has been added, which calculates Cu-speciation and predicts expected ranges of free  $Cu^{2+}$  ion concentrations.

The chemical fate modules in the MAM-PEC model are based on a 2D steady state version of DELWAQ (WL| Delft Hydraulics), a first order rate constant-based compartment modelling framework for water quality applied on a grid basis with variable spatial resolution. The UI software is programmed in VB4.0. User supplied information is stored in Access type database. MAM-PEC runs under Win95 on normal desktop or laptop PCs. The model has a Windows 'look and feel' and can be considered as user friendly.

For a selected number of compounds model-predictions for specific environments were compared with measured in order to evaluate the validity of the model. The model predictions appeared to be reasonably in line with results from monitoring studies.





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## Annex-1 Shipping categories according to the Lloyds system

Basic Grouping	Code	Shiptypes
<b>A. Cargo Carrying Ships</b>		
<i>1. Bulk Liquid Cargo Carrying Ships</i>		
Liquefied Gas	A110	Liquefied Gas Tanker, Liquefied Gas/Chemical Tanker
Chemical Tanker	A120	Chemical Tanker, Chemical/Oil Tanker
Oil Tankers	A130	Oil Tanker
Other Liquids	A140	Molasses Tanker, Bitumen Tanker, Vegetable Oil Tanker, Fruit Juice Tanker, Wine Tanker, Beer Tanker, Water Tanker
<i>2. Bulk Dry Cargo Carrying ships</i>		
Bulk Dry	A210	Bulk Carrier, Ore Carrier
Bulk Combination (Dry/Oil)	A220	Bulk/Oil Carrier, Ore/Oil Carrier
Self Discharging Bulk Dry	A230	Self-Discharging Bulk Carrier
Other Bulk Dry	A240	Cement Carrier, Wood Chips Carrier, Urea Carrier, Limestone Carrier, Refined-Sugar Carrier
<i>3. All Other Dry Cargo Carrying Ships (including passenger carriers)</i>		
General Cargo	A310	General Cargo Ship, Palletised Cargo Ship, Deck Cargo Ship
General Cargo/Passenger	A320	Passenger/General Cargo Ship
Container Ships	A330	Container Ship
Refrigerated Cargo	A340	Refrigerated Cargo Ship
Ro-Ro Cargo	A350	Ro-Ro Cargo Ship, Container/Ro-Ro Cargo Ship, Vehicles Carrier, Landing Craft
Passenger/Ro-Ro Cargo	A360	Passenger/Ro-Ro Cargo Ship, Passenger/Landing Craft
Passenger	A370	Passenger Ship
Other Dry Cargo	A380	Livestock Carrier, Barge Carrier, Heavy Cargo Carrier, Nuclear Fuel Carrier
<b>B. Ships of Miscellaneous Activities</b>		
<i>1. Fishing</i>		
Fishing Catching Vessels	B110	Trawler, Fishing Vessel
Other Fishing	B120	Fish Factory Ship, Fish Carrier, Live-Fish Carrier
<i>2. Offshore</i>		
Offshore Supply	B220	Offshore Supply Ship
Other Offshore	B220	Offshore Support Ship, Offshore Well Production Ship, Drilling Ship, Pipe-Laying Ship
Basic Grouping	Code	Shiptypes



Basic Grouping	Code	Shiptypes
<i>3. Other Miscellaneous Activities</i>		
Research Vessels	B310	Research Ship
Towing and Pushing	B320	Tug, Pusher Tug
Dredging	B330	Dredger, Hopper Dredger
Other Activities	B340	Motor Hopper, Sludge Disposal Vessel, Crane Ship, Cable Ship, Ice-Breaker, Fire-Fighting Ship, Pollution Recovery Vessel, Tender, Hospital Ship, Lifeboat, Launch

Source: Lloyds.

## Annex-2 Antifouled area of Reefers as function of deadweight (DWT)

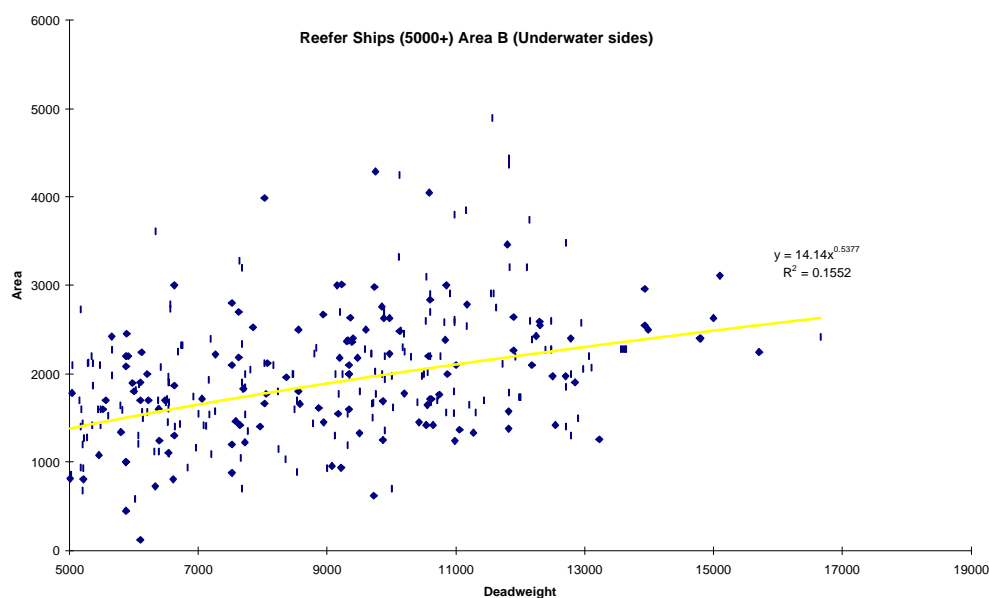


Figure A2.1 Reefer Ships ( $n=297$ ) - Antifouled area ( $m^2$ ) of flats as function of deadweight (DWT). Data from Akzo Nobel International.

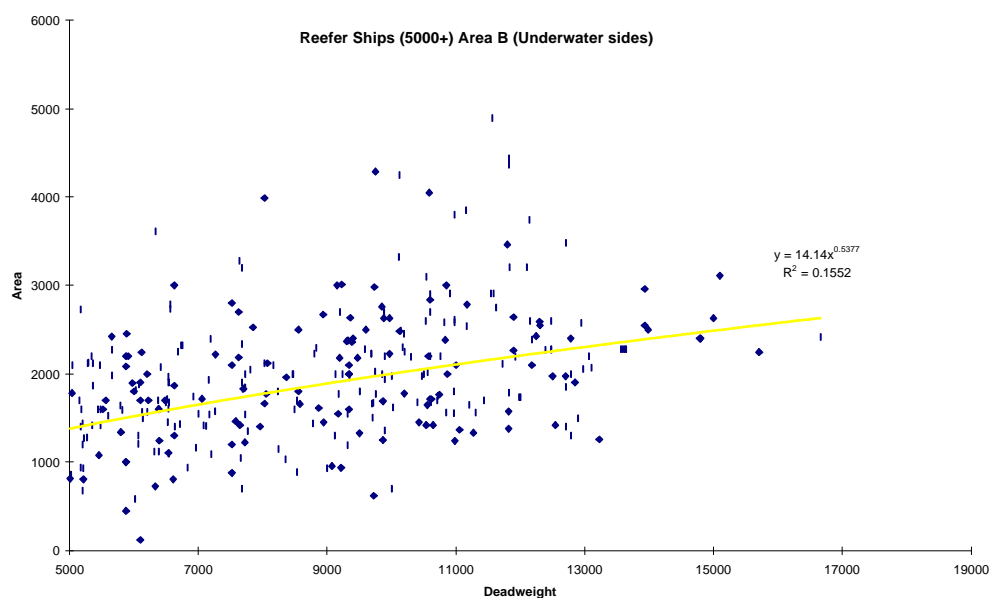


Figure A2.2 Reefer Ships ( $n=322$ ) - Antifouled area ( $m^2$ ) of undersides as function of deadweight (DWT). Data from Akzo Nobel International.

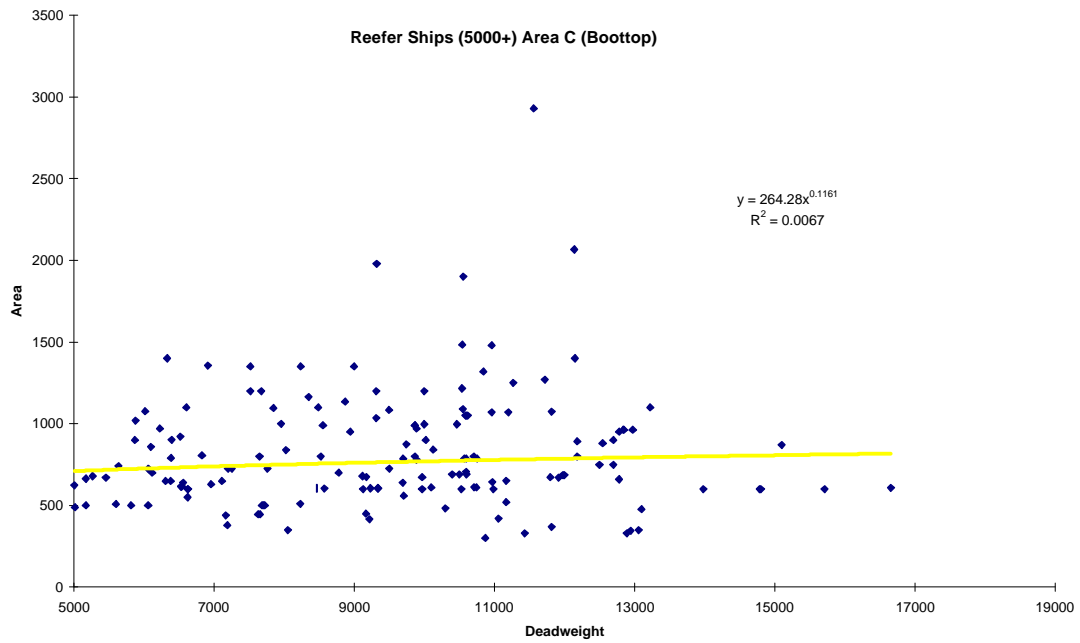


Figure A2.3 Reefer Ships ( $n=159$ ) - Antifouled area ( $m^2$ ) of boottops (area antifouled but not permanently immersed - the waterline area) as function of dead-weight (DWT). Data from Akzo Nobel International.

## Annex-3 Water exchange mechanisms

In general, the exchange of water between a harbour basin and an estuary is caused by three phenomena, that is by (Eysink and Verinaas, 1983; Eysink, 1988):

- filling and emptying by the tide;
- the horizontal eddy generated in the harbour entrance by the passing main flow; and
- vertical circulation currents in the harbour generated by density differences between the water inside and outside the basin.

In some cases the above picture is complicated by the extra effects of a water discharge through the harbour basin to the estuary or sea. On the one hand such a discharge has a positive effect by flushing the basin, but on the other hand it has a negative effect by introducing or enhancing water exchange by density currents. It even may introduce a serious sediment influx contributing to the shoaling in the harbour basin. This mechanism is addressed to as flushing with withdrawal of water (e.g. cooling water intake) defined as a negative flushing discharge rate.

The exchange by the first mechanism over a tidal periodin, i.e. the tidal prism can easily be determined as:

$$V_t = 2\eta A_b \quad (6)$$

where:

$V_t$  = tidal prism of the harbour basin

$\eta$  = tidal amplitude

$A_b$  = (storage) area of the basin.

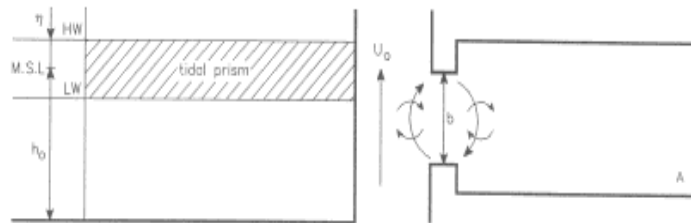


Figure A-3.1 Definition of tidal prism and horizontal exchange mechanism.

In the exchange module of MamPec the total water exchange volume is the sum of the tidal prism and the exchange volumes due to the horizontal eddy in the harbour entrance ( $V_h$ ), due to density currents ( $V_d$ ) and the extra water exchange due to flushing ( $V_{ef}$ ):

$$V_e = V_t + V_h + V_d + V_{ef} \quad (7)$$

The quantities  $V_h$ ,  $V_d$  and  $V_{ef}$  are less obvious than  $V_t$  and are dealt with in more detail in the next sections.

### Water exchange by a horizontal eddy in the harbour entrance

A current passing the entrance of a basin generates an eddy in this entrance (see Figure 2). There, steep velocity gradients generate an exchange of water by turbulence. Through this mechanism silt laden water from outside penetrates the eddy and from there further into the harbour and to the centre of the eddy. Thus, the silt reaches areas with weak flow velocities and insufficient turbulence to keep the sediment in suspension. Hence, sedimentation occurs.

The rate of water exchange by this mechanism depends on the flow velocity in front of the harbour basin, the size of the entrance and the tidal prism. It will be obvious that the rate of exchange decreases with increasing tidal prism. The rate of "horizontal water exchange" can be approximated by the formula (Graaf and Reinalda, 1977):

$$Q_h = f_1 \cdot h b \cdot u_0 - f_2 \cdot Q_t$$

where:

$Q_h$  = rate of horizontal water exchange

$f_1, f_2$  = empirical coefficients depending on the geometry of the basin

$h$  = depth of entrance

$b$  = width of entrance

$u_0$  = main flow velocity in front of the entrance

$Q_t$  = filling discharge due to rising tide ( $= h b \cdot u_t$ )

$u_t$  = tidal in- and outflow velocities in the entrance

This formula is valid for rivers ( $Q_t = 0$ ) and in tidal areas during flood;  $Q_h$  almost is negligible during ebb (Graaf and Reinalda, 1977). Hence, substitution of  $h = h_0 - \eta \cos \omega t$  and  $u_0 = u_{0,\max} \sin \omega t$  and integration over the flood period ( $t = 0$  to  $T/2$ ) yield the total volume per tide by horizontal exchange:

$$V_h = f_1 h_0 b - u_{0,\max} / \pi \cdot T - f_2 V_t$$

where:

$V_h$  = total volume of water exchange per tidal cycle by horizontal exchange flow

$h_0$  = depth in the entrance relative to MSL

$T$  = tidal period

$V_t$  = tidal prism of harbour basin

The coefficients  $f_1$ , and  $f_2$  generally are within the ranges 0.01-0.03 and 0.1-0.25 respectively and can be estimated based on existing knowledge from comparable situations. In some cases it may appear useful to determine more accurate values via hydraulic model investigations.

In case the equation yields a negative value for  $V_h$  it means that the horizontal exchange does not contribute to the total water exchange, in which case  $V_h = 0$ .

### Water exchange due to density currents

Water exchange is also caused by density differences between the water inside and outside the harbour basin. This mechanism is very effective and, besides, it affects the entire basin while the two others are restricted to the area near the entrance.

The water exchange due to the density currents is reduced by the tidal filling or emptying of the harbour basin.

The water exchange due to density currents is reduced by the tidal filling/ emptying of the harbour basin. This also applies to density induced exchange.

Relationships between relevant parameters as waterlevel variation at the harbour entrance ( $h$ ), river flow in front of it ( $U_0$ ), the mean density variation outside the harbour ( $\Delta_0$ ) and inside the harbour ( $\Delta_{ha}$ ) and their difference. And also the tidal in and outflow currents and the undisturbed and effective density current ( $U_{do}$  and  $U_t$ , respectively) can be described with harmonic functions.

Assuming linear harmonic relationships, the density induced exchange flow rate is integrated over a tidal cycle which yields

$$u_{do} = f_3 * (\Delta\rho / \rho * g * h)^{0.5}$$

$$V_d = f_{4,max} * h * b * (\Delta\rho_{max} / \rho * g * h_0)^{0.5} * T - f_5 * V_t$$

$$V_{d0} = f_{4,max} * h * b * (\Delta\rho_{max} / \rho * g * h_0)^{0.5}$$

$u_{do}$  = exchange velocity without influence of tidal in- and outflow

$\rho$  = density of water

$\Delta\rho$  = characteristic density difference

$f_3$  = coefficient

$V_d$  = exchange volume per tide due to density currents

$f_4$  = coefficient depending on  $V_{do}/V_{ha}$  with  $V_{ha}$  being the volume of the basin below MSL (mean sea level)

$f_5$  = coefficient depending on  $V_{do}/V_{ha}$  and the phase lag between  $U_{do}$  and  $U_t$

In large harbours (low values of  $V_{do}/V_{ha}$ ) the average water density will hardly follow the density fluctuations of the water in front of the harbour. In case of a small harbour basin or strong density currents the density of the inside the harbour may follow density fluctuations outside. This results in a reduction of the characteristic density difference inducing the density currents. This effect is included in coefficient  $f_4$ . This effect has been estimated theoretically on basis of linear harmonic theory (Silthar - manual)

### Additional water exchange due to flushing

In some cases water is withdrawn from a harbour (e.g. for cooling water; intake harbour) or water is discharged into it (e.g. drainage water, small river). In one way or another this affects the water exchange rate of the harbour basin.

If water is withdrawn from the harbour or if water with the same density is released into it, no other density currents will occur than those generated by fluctuations of the water density in front of the harbour entrance. The flushing discharge in the first place affects the flow velocities in the harbour entrance due to tidal filling and emptying of the basin and, hence, the tidal prism. Through this it also affects the two other water exchange mechanisms.

If water with a different density is discharged into the harbour basin the situation becomes more complex. In general, the water will partly mix by entraining water from the basin and a three-layer system may occur in the harbour. This also affects all other water exchange mechanisms.

The additional water exchange due to flushing with a constant discharge rate can be fairly well approximated in a theoretical way (see Silthar manual ).

Note: References in Appendix III as cited in WL, 1995.

Annex-4 Compound property input data (defaults in model)<sup>1)</sup>

CmpID CmpDescr	1 (new)	161 Copper (total)	182 Dichlofluanid (default)	183 Tolylfluanid (default)	184 Zinc Omadine (default)	185 Diuron (default)	186 Irgarol (default)	187 Seanine (default)	188 TBT <sup>2)</sup> (default)
CmpName	new	Copper	Preventol A4S	Preventol A5S	Zinc-pyrithione	Preventol A6	Irgarol	Seanine	TBT
CmpIsType	3	2	3	3	3	3	3	3	3
CmpIsCopper	FALSE	TRUE	FALSE	FALSE	FALSE	FALSE	FALSE	FALSE	FALSE
CmpMolmass	100	63.5	333.2	347.3	317.7	233.1	253.37	282	290.04
CmpVappress	1E-10	0	2.15E-05	0.0002	0.000001	2.3E-07	0.000088	4.5E-06	0.000085
CmpSol	1	0.001	1.3	0.9	6	35	7	4.7	1.9
CmpKow	1	0	3.7	3.9	0.93	2.82	2.8	2.85	3.8
CmpKd	0	30	0	0	0	0	0	0	0
CmpKoc	1	0	3.13	3.35	3	3.4	3.1	4.19	4.6
CmpKdoc	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
CmpBcf	1	0	0	0	0	0	0	0	0
CmpH	1	0	0.0055	0.077	0.00005	1.53E-06	0.00319	6E-09	0.02
CmpTmelt	1	0	103.2	93	260	156	130	41	0
CmppKa	14	0	14	14	0	14	5.16	14	0
CmpDegrBiowater	0	0	5.54 <sup>5)</sup>	2.77 <sup>4)</sup>	2.08	0.022	0.028	16.5	0.041
CmpDegrHydwater	0	0	13.86 <sup>6)</sup>	8.3	0.054	0	0	0.05	0
CmpDegrPhowater	0	0	0	0	5.5 <sup>3)</sup>	0	0	0	0
CmpDegrBioSed	0	0	0.69 <sup>5)</sup>	3.47 <sup>4)</sup>	7.9	0	0.028	16.5	0.0014
CmpDegrHydSed	0	0	0	0	33	0	0	0	0
CmpDegrPhoSed	0	0	0	0	0	0	0	0	0

<sup>1)</sup> Generic values provided by participants of CEPE-AWG, unless indicated otherwise; <sup>2)</sup> From Stronkhorst *et al.* (1996); <sup>3)</sup> 24-hour averaged photolysis rate over a 3.0 meter water column, where irradiance (330-800 nm) = 154 W/m<sup>2</sup>, Diffuse optical attenuation coefficient = 3.45 and surface photolysis rate = 56.9 day<sup>-1</sup>. <sup>4)</sup> Bayer AG (2002b). <sup>5)</sup> Bayer AG (2002a) <sup>6)</sup> Hydrolysis rate constant has dependency on pH and temperature.



**Explanation of symbols**

Parameter	Symbol	Unit
Compound class	CmpIsType	-
Molecular mass	CmpMolmass	g/mol
Vapour pressure	CmpVappress	Pa
Solubility	CmpSol	g/m <sup>3</sup>
Octanol-water partitioning coefficient	CmpKow	- as Log K <sub>ow</sub>
Sediment-water distribution coefficient	CmpKd	m <sup>3</sup> /kg
Organic carbon adsorption coefficient	CmpKoc	L/kg oc as Log K <sub>oc</sub>
Henry's Law constant	CmpH	Pa.m <sup>3</sup> /mol
Melting point	CmpTmelt	°C
Acid dissociation constant pKa	CmppKa	-
Biotic degradation rate constant (water)	CmpDegr Biowater	day <sup>-1</sup>
Hydrolysis rate constant (water)	CmpDegr Hydwater	day <sup>-1</sup>
Photolysis rate constant (water)	CmpDegrPhot	day <sup>-1</sup>
Sediment biotic degradation	CmpDegrBioSed	day <sup>-1</sup>
Sediment abiotic degradation rate constant	CmpDegrHydSed	day <sup>-1</sup>

**Note:**

It should be noted that the values are recommended generic values, based on the current information provided by participants in the CEPE AFWG. Some properties (e.g. K<sub>ow</sub>, photolysis, hydrolysis, biodegradation) may be habitat-specific and dependent on salinity, temperature, pH or other environmental factors..

It is the responsibility of the user or risk-assessor to select the most appropriate parameter values for the model-scenarios considered.

## Annex-5 Settings for default environments in model and validation chapter

ID	1	70	62	38	71	37	40
Description	(new)	Default commercial harbour	Default estuarine harbour	Default marina	Default marina 400m poorly flushed	Default shipping lane	Default open sea
Type	New	Com	Est	Mar	Mar	Sea	Sea
Silt	35	35	35	35	35	5	5
POC	1	1	1	1	1	0.3	0.3
Temperature	15	15	15	20	15	15	15
Salinity	34	30	34	34	34	34	34
pH	8	7.5	7.5	8	8	8	8
Conc	0	0	0	0	0	0	0
x1	1000	2000	1000	400	400	20000	20000
x2	1000	10000	5000	400	400	0	0
y1	1000	2000	1000	400	400	10000	10000
y2	1000	500	500	400	400	0	0
Depth	10	20	15	3.5	3.5	20	20
Mouth	1000	5000	2500	100	50	0	0
MouthDepth	10	20	15	3.5	3.5		
Flow	1	1.5	1	1	0.2	1	1
Flush	0	0	0	0	0	0	0
Tide	1.5	1.5	1.5	1	0	0	0
DensDif	0	0.8	0.4	0.1	0	0	0
FlushDensDif	0	0	0	0	0	0	0
TidalPeriod	12.41	12.41	12.41	12.41	12.41	12.41	12.41
MouthArea	5000	100000	37500	350	175	0	0
HeightDam	0	0	0	0	0	0	0
WidthDam	0	0	0	0	0	0	0
SeaX	0	0	0	0	0	10000	10000
SeaY	0	0	0	0	0	20000	20000
SeaDepth	0	0	0	0	0	20	20
SeaFlow	0	0	0	0	0	1	1
Exchange	34000	2.59E+08	60262000	243420	9954.6	1500	1500
NettSedimentationVelocity	0.2	1	1	0.5	1	0.2	0.2
DepthSedimentLayer	0.1	0.2	0.2	0.1	0.1	0.1	0.1
RhoSediment	1000	1000	1000	1000	1000	1000	1000
FractionOCSediment	0.028	0.03	0.03	0.03	0.03	0.01	0.01
DOC	2	2	2	2	2	0.2	0.2

## Annex-6 Default emission scenarios in model, used for validation chapter

[illegible]

[illegible]

[illegible]

## Annex-7 Model runs with default scenarios used in the validation section

RunDescription	(new)	Default commercial harbour TBT (default) Default Commercial Harbour TBT 100%	Default estuarine harbour TBT (default) Default Estuarine Harbour TBT 100%	Default marina TBT (default) Default Marina TBT 100%	Default marina TBT (default) Default Marina TBT 20%	Default shipping lane TBT (default) Default Shipping Lane TBT 100%	Default open sea TBT (default) Default open sea TBT 100%	Default marina Irgarol (default) Default Marina biocide 100 %	Default marina 400m poorly flushed Irgarol (default) Default Marina biocide 100 %	Default commercial harbour Copper (total) Default Commercial Harbour Cu 100%	Default marina Copper (total) Default Marina Cu 100%
EnvirID	1	70	62	38	38	37	40	38	71	70	38
CompoundID	1	188	188	188	188	188	188	186	186	161	161
EmisID	1	65	48	55	59	50	58	57	57	67	68
ConcMax	0	0.738736	0.296624	0.233441	0.046688	0.000691	1.6E-05	0.146548	1.613315	9.764545	2.896291
Conc95	0	0.732503	0.291276	0.223235	0.044647	0.000632	1.46E-05	0.140126	1.613277	9.686626	2.77017
ConcAve	0	0.244168	0.103887	0.160711	0.032142	0.000110	2.54E-06	0.100955	1.139046	3.210855	1.991771
ConcMedian	0	0.033217	0.027457	0.164042	0.032808	0.000138	3.19E-06	0.103083	1.08634	0.417749	2.031857
ConcMin	0	0.005329	0.004001	0.035048	0.007010	0.000001	2.34E-08	0.022026	0.513549	0.066701	0.434035
FNameMap	dummy.map	dummy.map	dummy.map	dummy.map	dummy.map	dummy.map	dummy.map	dummy.map	dummy.map	dummy.map	dummy.map
FNameRank	dummy.rnk	dummy.rnk	dummy.rnk	dummy.rnk	dummy.rnk	dummy.rnk	dummy.rnk	dummy.rnk	dummy.rnk	dummy.rnk	dummy.rnk
ConcMaxDis	0	0.702385	0.282028	0.221954	0.044391	0.000682	1.58E-05	0.146309	1.610679	4.763193	1.412825
Conc95Dis	0	0.696459	0.276943	0.21225	0.04245	0.000624	1.44E-05	0.139897	1.610641	4.725184	1.351302
ConcAveDis	0	0.232154	0.098775	0.152803	0.030561	0.000108	2.5E-06	0.10079	1.137185	1.566271	0.971596
ConcMedianDis	0	0.031582	0.026106	0.15597	0.031194	0.000136	3.15E-06	0.102914	1.084565	0.20378	0.99115
ConcMinDis	0	0.005067	0.003804	0.033323	0.006665	9.99E-07	2.31E-08	0.02199	0.51271	0.032537	0.211724
ConcMaxAds	0	27.96244	11.22774	8.836155	1.767231	0.027135	0.000627	0.184192	2.027725	142.8958	42.38474
Conc95Ads	0	27.72651	11.02531	8.44984	1.689968	0.024828	0.000574	0.17612	2.027676	141.7555	40.53907

RunDescription	(new)	Default commercial harbour TBT (default) Default Commercial Harbour TBT 100%	Default estuarine harbour TBT (default) Default Estuarine Harbour TBT 100%	Default marina TBT (default) Default Marina TBT 100%	Default marina TBT (default) Default Marina TBT 20%	Default shipping lane TBT (default) Default Shipping Lane TBT 100%	Default open sea TBT (default) Default open sea TBT 100%	Default marina Irgarol (default) Default Marina biocide 100 %	Default marina 400m poorly flushed Irgarol (default) Default Marina biocide 100 %	Default commercial harbour Copper (total) Default Commercial Harbour Cu 100%	Default marina Copper (total) Default Marina Cu 100%
ConcAveAds	0	9.242199	3.93232	6.083207	1.216641	0.004313	9.97E-05	0.126887	1.43163	46.98813	29.14787
ConcMedianAds	0	1.257316	1.039304	6.209276	1.241855	0.005422	0.000125	0.129561	1.365386	6.113405	29.7345
ConcMinAds	0	0.201731	0.151437	1.32663	0.265326	3.98E-05	9.19E-07	0.027684	0.645464	0.976119	6.351733
BackConc	0	0	0	0	0	0	0	0	0	0	0
MaxConcAds1	0	1.35843	0.54545	0.429265	0.085853	7.74E-05	1.79E-06	0.001144	0.025033	8.842069	2.622672
MaxConcAds2	0	2.122921	0.852415	0.670845	0.134169	0.000124	2.86E-06	0.001144	0.025034	17.13701	5.083059
MaxConcAds5	0	2.931547	1.177102	0.926371	0.185274	0.000178	4.11E-06	0.001144	0.025034	39.06728	11.58786
MaxConcAds10	0	3.097037	1.243551	0.978666	0.195733	0.000191	4.42E-06	0.001144	0.025034	67.45368	20.00763
MaxConcAds20	0	3.106906	1.247514	0.981785	0.196357	0.000192	4.45E-06	0.001144	0.025034	103.066	30.5707
MaxConcAds50	0	3.106938	1.247527	0.981795	0.196359	0.000192	4.45E-06	0.001144	0.025034	137.0345	40.64621
MaxConcAds100	0	3.106938	1.247527	0.981795	0.196359	0.000192	4.45E-06	0.001144	0.025034	142.6554	42.31343
AveConcAds1	0	0.448991	0.191034	0.295525	0.059105	1.23E-05	2.84E-07	0.000788	0.017674	2.907519	1.803604
AveConcAds2	0	0.701672	0.298543	0.46184	0.092368	1.97E-05	4.54E-07	0.000788	0.017674	5.635128	3.495605
AveConcAds5	0	0.96894	0.412259	0.637756	0.127551	2.83E-05	6.53E-07	0.000788	0.017674	12.84641	7.968939
AveConcAds10	0	1.023638	0.435532	0.673758	0.134752	3.04E-05	7.03E-07	0.000788	0.017674	22.18065	13.75919
AveConcAds20	0	1.026901	0.43692	0.675905	0.135181	3.06E-05	7.07E-07	0.000788	0.017674	33.89097	21.02339
AveConcAds50	0	1.026911	0.436924	0.675912	0.135182	3.06E-05	7.07E-07	0.000788	0.017674	45.06078	27.95229
AveConcAds100	0	1.026911	0.436924	0.675912	0.135182	3.06E-05	7.07E-07	0.000788	0.017674	46.90907	29.09883
MedianConcAds1	0	0.061081	0.05049	0.30165	0.06033	1.55E-05	3.57E-07	0.000805	0.016856	0.378284	1.839904
MedianConcAds2	0	0.095456	0.078904	0.471411	0.094282	2.47E-05	5.71E-07	0.000805	0.016857	0.73316	3.565958
MedianConcAds5	0	0.131815	0.108959	0.650973	0.130195	3.55E-05	8.21E-07	0.000805	0.016857	1.671386	8.129322

[illegible]



## Annex-8 Model settings for European marinas

Marina	IJmuiden NL	Fiskebäckskil Marina. SW	EGAA Ma- rina DK	Igoumenitsa GR	Arcachon F	Marseille F	Sutton Ma- rina UK
<b>Water characteristics</b>							
Silt	35	35	10	5	4	4	150
POC	1	0.59	1	0.3	0.4	0.4	6
DOC	1	1	1	1	1	1	1
Temperature	15	17	15	17	15	26	15
Salinity	34	23	20	36	25	38	34
pH	8	8	8	7.8	8	8	8
Conc	0	0	0	0	0	0	0
<b>Sediment</b>							
Nett sedimentation ve- locity	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Depth sediment Layer	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Density of sediment	1000	1000	1000	1000	1000	1000	1000
Org-C sediment	0.03	0.03	0.03	0.03	0.03	0.03	0.03
<b>Harbour lay-out and exchange</b>							
x1	24	100	100	150	400	400	100
x2	240	230	400	300	400	400	600
y1	240	950	175	200	400	800	700
y2	24	100	100	150	400	400	100
Depth	6	4.3	4	3.5	4	5	3
Mouth	30	170	30	100	100	100	7
MouthDepth	6	4	4	3.5	4	5	3
Flow	0	0.25	0.1	0.09	0	1	0
Tide	1.5	0.17	0.3	0.4	5	0.2	0.5
DensDif	0	0	0	0	0	0	0
TidalPeriod	12.41	12.41	12.41	11	12.41	12.41	12.41
MouthArea	180	680	120	350	300	500	21
HeightDam	0	0.3	0	0	1	0	0
WidthDam	0	170	0	0	100	0	0
Echange % per tide	25%	8%	8%	13%	125%	12%	17%
<b>Emission</b>							
Nr of ships <10 m	150	-	300	300	2000	500	-
Nr of ships 10-50m	150	400	-	-	300	2500	300
Area <10 m	10	-	20	8	7.5	7.5	-
Area 10-50m	25	25	-	-	15	25.5	15
Leaching rate	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Application factor	20%	20%	80%	20%	20%	20%	50%
Emission load g/day	26	50	120	12	98	338	56

Marina	IJmuiden NL	Fiskebäckskil Marina. SW	EGAA Ma- rina DK	Igoumenitsa GR	Arcachon F	Marseille F	Sutton Ma- rina UK
<b>PEC water (ng/L)</b>							
Conc Max	38	224	573	86	56	296	35
Conc 95	38	224	567	86	54	295	35
Conc Ave	29	124	469	56	45	195	29
Conc Median	29	113	470	53	46	189	30
Conc Min	11	25	248	17	28	51	15